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Application of Adsorptive/Absorptive Resins and Membranes for Toxic and Hazardous Waste Reduction

Carltech Associates, Columbia, MD

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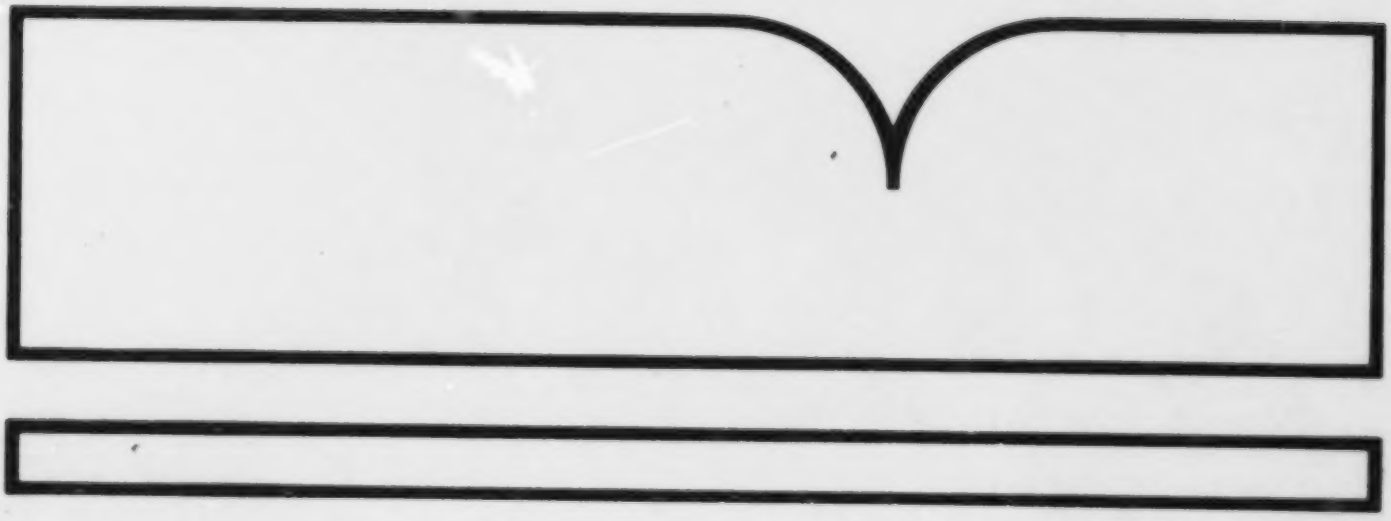

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APPLICATION OF ADSORPTIVE/ABSORPTIVE RESINS AND MEMBRANES FOR TOXIC AND HAZARDOUS WASTE REDUCTION

by

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16. ABSTRACT

An extensive review of the literature has been performed which included recent papers prepared by experts from industry, government and academia in the fields of ion exchange, reverse osmosis, ultrafiltration and many associated technologies. The capabilities of adsorptive and ion exchange systems using conventional resins as well as the newer ion-selective and macroreticular non-ionic resins are presented. The capabilities of membrane separation processes based on the use of conventional size exclusion and ion exchange film type membranes and experimental liquid membranes are similarly evaluated.

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This study reviews the state-of-the-art for potential applications of adsorptive/absorptive ion exchange resins and membrane technology to reduce toxic and hazardous waste releases to the environment. For further information on toxic waste controllability, contact should be made with the Industrial Wastes and Toxics Technology Division, Water Engineering Research Laboratory, Cincinnati, Ohio.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

The state of the art of commercially available and developmental membrane separation and ion exchange/adsorption resin technologies is assessed to determine their potential for reducing or eliminating hazardous materials from the liquid wastes generated in the metals finishing and munitions manufacturing industries. The study involved an extensive review of the literature including recent papers prepared by experts from industry, government and academia in the fields of ion exchange, reverse osmosis, ultrafiltration and many associated technologies. Additional data were obtained through direct interviews with leading researchers in this rapidly developing scientific field. The capabilities of adsorptive and ion exchange systems using conventional resins as well as the newer ion-selective and macroreticular non-ionic resins are presented. The capabilities of membrane separation processes based on the use of conventional size exclusion and ion exchange film type membranes and experimental liquid membranes are similarly evaluated.

The process streams and operations involved in the metal finishing and munitions manufacturing industries were studied in detail and all of the important chemical species normally found in aqueous solutions throughout the plants were identified. Other chemical and physical characteristics of these streams such as the pH level, the amount of suspended solids present, and the presence of strong oxidizing or reducing agents, are also documented. The treatment problems encountered in the two industries are quite different since the species to be removed in the metal finishing industry wastes are primarily ionic while the wastes from the munitions industry contain mostly non-ionic nitrated organic compounds. Both membrane separation and ion exchange/adsorption resin systems are evaluated relative to the specific characteristics of the hazardous materials to be removed from these diverse waste streams and to the adverse or harsh chemical/physical conditions that may be encountered in treating wastes from the target industries.

This report was submitted in fulfillment of Military Interdepartmental Purchase Request Number D-4-78-11 by the U.S. Environmental Protection Agency under the sponsorship of the U.S. Army Toxic and Hazardous Materials Agency.

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SECTION I

INTRODUCTION

The state of the art of commercially available and developmental membrane and resin technologies was assessed for applicability to treatment of toxic and hazardous wastes generated by metal finishing and munitions manufacture. The information in this report was obtained from interviews with and recent papers written by experts in their respective fields. Experts included members of industry, government and academia. Information on specific products was supplied by their manufacturer and claims of performance made by these manufacturers must be substantiated. In this introductory section, the types of wastes that are particular to the metal finishing and munitions industry will be discussed.

TOXIC AND HAZARDOUS WASTES IN THE ELECTROPLATING AND METAL FINISHING INDUSTRY

It has been estimated that the metal finishing industry utilizes more than one hundred surface finishing and fabricating processes that require aqueous applications and removals of various metals to and from metallic and plastic parts.[1] The electroplating industry was examined and a list developed of species of interest. Included were the cationic metals that are involved in various types of electroplating: baths used in the manufacture of vehicles; the manufacture of printed circuit boards; and other finishing of industrial metals. In most electroplating operations, various organic compounds are used to clean and brighten the metal. Chelates are also used. Unfortunately, the identities of these organic compounds are often considered proprietary information, although it is known that some of the simple additives include EDTA, formaldehyde, and saccharin.[2]

While this study concentrated on electroplating, other areas of metals finishing will be noted where the nature of the problems and solutions are similar. The interest in cleanup of electroplating wastes is a result of the following:

- Restrictions of the levels of toxic materials in the wastewaters from metals finishing plants brought about by effluent limitations under the Clean Water Act
- The limitations on metals imposed by the U.S. Public Health Service are currently under review and probable tightening up by the EPA's Office of Drinking Water
- The economic incentive to recover valuable metals at the source rather than dispose of them in the form of a toxic or hazardous sludge
- The potential for recovery and reuse of water.

The plating industry itself has two major sources of wastewater. One is the spent plating bath or, in some instances, the anodizing bath. The other is the rinse waters which are essentially diluted plating or anodizing solutions. These waste streams may be quite varied in composition.

HAZARDOUS WASTES IN THE MUNITIONS INDUSTRY

The hazardous waste problems of the munitions industry were examined. The preliminary list of possible hazardous species developed at the beginning of the project included explosives used both by the military and non-military munitions industries. Common explosives contain nitro groups, (NO_2), attached to a wide variety of structures which can be aromatic (benzene ring type), heterocyclic (rings containing non-carbon atoms), or aliphatic (straight or branched chains). TNT (trinitrotoluene) and picric acid are examples of aromatic nitro compounds. RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), SEX (1-Acetyl-1,2,3,4,5, 6,7,8-octahydro-3,5,7-trinitro-1,3,5,7-tetrazocine), and TAX (1-Acetyl-1,2,3,4,5,6-hexahydro-3,5-dinitro-1,3,5 triazine) are heterocyclic nitro compounds. PETN (pentaerythritol tetranitrate) is an aliphatic nitro compound.

The munitions industry also produces organic and inorganic salts of lead and mercury as initiators of the explosion process. Some common initiators, or primers are high order explosives, as are the compounds listed above. Additionally, primers are extremely sensitive to heat, shock, or friction and will explode violently.

The military munitions industry has a particular problem with the effluent from LAP (load, assembly, and pack) plants where artillery shells are cleaned and repacked with fresh explosives. Steam is used throughout the operation, generating a waste stream high in dissolved organics. This waste stream contains TNT, RDX, and HMX and is also called "pinkwater," because of its highly colored complexes. This aqueous solution must be treated before discharge.

There is really no comparable industry outside the non-military explosives industry in terms of toxic and hazardous waste. The munitions industry is unique in the amount of nitrated aromatic compounds used and the inherent danger associated with them.

USE OF RESIN SYSTEMS

Information on new ion selective resin technologies for treatment of electroplating and munitions toxic and hazardous wastes was considered for this study. The phrase "ion-selective resin technologies" are discussed in order to properly identify the materials that have been considered.

Conventional ion exchange resins may be regarded as three dimensional bead structures to which an exchangeable ion has been attached. The most common currently used resins have polystyrene crosslinked by varying amounts of divinylbenzene (DVB) as the insoluble polymer matrix. There are other such structures, however, that are less commonly used. For example, the first

synthetic ion exchangers were based on the phenol-formaldehyde reaction. In some of the commercially available resins today, the polymer matrix consists of methacrylic or acrylic acid crosslinked with DVB or the condensation product of epichlorohydrin with anions. A number of other types of polymer matrices that have been developed for specific ion removal purposes will be described.

USE OF MEMBRANE SYSTEMS

The use of membrane technology for industrial purposes involving aqueous wastes has been commercially possible for about the last 30 years. Traditionally, a membrane was defined as a thin pliable sheet or layer that allowed one component of a solution to pass through while preventing others. As knowledge increases, the definition is being broadened. This report will use Strathmann's definition:[21] "A membrane is an interphase which separates two phases and restricts the transport of various chemical species in a rather specific manner."

Membranes are currently used or are being developed for use in the following industries:

- Medicine (especially in hemodialysis)
- Pharmaceuticals (controlled release formulations and sterile solutions)
- Water conservation (desalination of sea and brackish water)
- Food and dairy industries
- Gas separations
- Paper industry (waste streams).

There have been three problems associated with membranes that have prevented their wider use in the industrial market. They are:

- Low flux through the membranes
- Fouling and adsorption on the membrane skin which lowers the flux
- Low resistance to harsh chemical environments such as very high or very low pH and to high temperatures.

New applications have been made possible by advances in membrane technology including:

- The formation of new polymers and novel membrane materials which can be operated over a broad range of pH and temperature

- The development of a fundamental understanding of the mechanisms of transport across membranes

- The development of thin-film composite membranes with insignificant compaction problems.

SECTION II

CONCLUSIONS

METALS FINISHING WASTE TREATMENT

Use of Ion Exchange Technology

Ion exchange resin technology is a mature technology for the removal of contaminants from plating solutions, the recovery of precious metals and the freshening of plating baths for reuse. This technology is being used both by manufacturers and by firms that collect and rejuvenate spent solutions from small companies. Research is being performed by private industry and government on process improvements in areas such as producing more highly selective resins and developing better removal and recovery techniques. The economics of using ion exchange technology in the treatment of these wastes varies widely for specific applications depending on the type of plating system involved and the configuration of rinses as well as the configuration of the waste treatment system.

Use of Membrane Technology

Reverse osmosis and ultrafiltration are mature technologies for treatment of metals finishing wastes. Zero sludge and reduced sludge systems are available and are used extensively throughout the industry. Reverse osmosis has a particularly high utilization rate in the treatment of nickel plating wastewaters.

Although zirconium oxide dynamic membranes are commercially available and appear promising, they have not been used to any extent in the treatment of hazardous wastes.

The newer membrane separation systems based on liquid and ion exchange membranes, Donnan dialysis, and emulsion type liquid membranes, are not sufficiently developed to assess their potential for application to the treatment of hazardous wastes.

In general the economics of using membrane separation systems in the treatment of these wastes depends on:

- The amount of water to be treated
- The fouling index (SDI) of the water to be treated
- Pretreatment requirements for the wastewater prior to introduction to the membrane separation process
- The potential for resource recovery.

Potential savings and capital payback depend on:

- The value of recovered materials
- The potential for reusing the treated water in the process
- Potential reductions in sewer discharge charges
- Potential savings in sludge removal and disposal charges.

Electrodialysis has been used to a moderate degree in the treatment of these waste streams. Other electrolysis processes have also been used to a moderate degree. Supported liquid membranes have been demonstrated in the field and show some promise and the combination of Donnan dialysis with other technologies has demonstrated potential for the treatment of these wastes. However, there is insufficient data available at this time to assess the potential economics of these systems in the treatment of metals finishing wastes.

Hexavalent chromium is probably the most difficult material to treat of the various pollutants from electroplating processes since it is an anion and a powerful oxidizing agent. Claims of successful treatment have not been fully substantiated by the data available at this time.

MUNITIONS WASTES TREATMENT

Use of Ion Exchange/Adsorption Resin Technology

Granular activated carbon (GAC) has been shown to be more cost effective in the treatment of munitions wastes than currently available macroreticular resins. However, recent laboratory studies indicate that the use of these resins in a two bed system has significant potential for being more cost effective than GAC in the future.

Use of Membrane Technology

There has been very little effort to apply membrane separation technology to the treatment of wastewaters from the munitions manufacturing industry. Concern over the potential for accumulating dangerous concentrations of explosive materials has been a major impediment to research in this area. Also, very little work has been undertaken on the application of membrane separation technology for treating the unique wastes from military installations. Although the data available indicate mixed results, this technology is considered to have a high potential for the treatment of these wastes in the future.

SECTION III

RECOMMENDATIONS

METAL FINISHING WASTE TREATMENT

Ion Exchange Technology

Bench scale screening studies are recommended to assess the performance of:

- New removal and regeneration techniques (e.g., countercurrent, monobeds and variations thereof) for the treatment of metals finishing wastes
- Existing ion specific resins (e.g., Amberlite 200, 400) for treatment/recovery from specific types of plating baths, rinses and other waste streams found in the electroplating industry
- Organic adsorption resins for metal selectivity.

Membrane Separations Technology

Engineering studies are recommended to evaluate the economics of treatment systems which combine membrane technology with chemical precipitation. These studies are recommended for plants where reduced sludge is an acceptable alternative or where the effluent stream is a mixture of wastes at the end of the pipe.

Pilot plant tests are recommended to evaluate the performance of membrane separation systems on:

- Metal finishing wastes containing chelates
- Chromium bearing wastes using reverse osmosis (e.g., Osmonics), COPS type systems (e.g., Nafion) and coupled transport liquid membranes (e.g., Bend Research) as the candidate technologies.

Screening at the bench scale level is recommended with existing liquid membranes for potential application in the treating of electroplating wastes. Support of basic research for the development of novel liquid membranes to treat specific types of electroplating wastes is also recommended.

MUNITIONS WASTES TREATMENT

Ion Exchange/Adsorption Resins Technology

Engineering studies are recommended to evaluate the following:

- The economics of alternatives to the regeneration (such as biological treatments or the use of precoats) of macroreticular resins (e.g., Amberlite XAD-2 or XAD-4) which have shown potential for the treatment of pinkwater

- The potential economics of two-bed systems (resin followed by activated carbon) for use in planning additional pilot plant studies.

Screening studies at the bench scale level are recommended for powdered precoats to enhance resin treatment performance in the following configurations:

- Powdered precoats alone

- Powdered precoats followed by resins

- Powdered precoats followed by activated carbon.

Basic research is recommended to develop new, higher capacity and more stable macroreticular resins, with the potential to remove specific contaminants from munitions wastes.

Membrane Separation Technology

Engineering studies are recommended to evaluate:

- The risk of explosions and other potential hazards when aqueous munitions wastes are concentrated

- The economics of membrane separation technologies combined with the use of activated carbon to pretreat LAP wastewaters; this system would separate TNT related hazardous materials from RDX related materials prior to treatment with GAC.

The following basic membrane research is recommended:

- Preliminary tests to quantify explosion and other hazards associated with the concentration of munitions wastes

- Preliminary tests with both noncellulosic and inorganic membrane materials to confirm expected resistance to deterioration when treating munitions waste streams

- Testing of membrane modules of various configurations to evaluate proposed new anti-fouling designs; these tests should be conducted using flow velocities similar to those used in large scale commercial installations

- Laboratory experimentation with novel liquid membranes with the potential for facilitated transport of organic munitions compounds

- The development of new membranes for selective separation of munitions organic wastes from high salt (high osmotic pressure) solutions.

SECTION IV

METHODOLOGY

SOURCES OF INFORMATION

A list was developed of separation science experts in industry, government, and academia. (Table 1). The 1984 SUR/FIN Conference of the American Electroplaters Society and the American Chemical Society Chemical Meeting were attended and experts were interviewed there. Finally, referrals were made by experts to other knowledgeable individuals. A list of key contacts showing both companies and individuals is presented in Table 2 (A, B1, & B2).

TELEPHONE INTERVIEWS

Telephone interviews were conducted and the following questions were asked:

- Have you or your company worked, or are you currently working in membrane/ion exchange resin research in the areas of metals finishing or the munitions industries?
- Do you know what companies or other individuals are in this area?
- Briefly, describe your work and send a copy of any papers, technical reports, or technical product information.

Memoranda were written on extensive conversations and publications were collected for analysis.

This list grew to almost one hundred companies or individuals. Listings were assigned a priority rank. Any individual who had published an article in the field or was referred to by other knowledgeable individuals, or was cited in the literature, was assigned top priority.

TRAVEL

The plants and research laboratories of various companies involved in membrane or ion exchange technology were visited. Interviews with knowledgeable individuals were conducted and the research and development of new membrane technology was discussed.

TABLE 1

SOURCES REVIEWED TO IDENTIFY KEY CONTACTS

MEMBRANE AND SEPARATION TECHNOLOGY NEWS, 1984
January - August, A.W. Crull, editor;
Business Communications Company, Inc.,
Stamford, CT

MEMBRANE AND SEPARATION PATENT SOURCEBOOK 1984
A.W. Crull, editor; Business Communications Co., Inc.,
Stamford, CT

CHEMICAL ENGINEERING EQUIPMENT BUYERS' GUIDE 1984
CHEMICAL ENGINEERING July 1984, McGraw Hill Inc.,
New York, NY

PRODUCTS FINISHING 1984 Directory, September 1983
Gardner Publications, Inc., Cincinnati, OH

METAL FINISHING June 1984, Metals and Plastics
Publications, Inc., Hackensack, NJ

1984 THOMAS REGISTER 73rd Edition, 1983,
Thomas Publishing Company, New York, NY

CONFERENCE PROGRAM, American Electroplating Society
Surface Finishing, New York, NY July 1984

TABLE 2

LIST OF TOP PRIORITY CONTACTS

A. Membrane Technology

Name	Company	Location
Alan S. Michaels	ALAN S. MICHAELS	New York, NY
Paul Tiegue	ABCOR	Wilmington, MA
Ken Manson	AMICON CORP.	Danvers, MA
James Szachta	APG CHEMICAL SYSTEMS	Aberdeen, MD
Henry K. Law	BELL LABS	Murray Hill, NJ
W.C. Babcock	BEND RESEARCH	Bend, OR
Gary Warga	CHEMAPEC	Woodbury, NY
Harry F. Gregor	COLUMBIA UNIVERSITY	New York, NY
Art Epstein	DORR OLIVER	Stanford, CT
Dale Eichenberg	DOW	Midland, MI
Irving Moch	DUPONT	Wilmington, DE
D. Furukawa	FILM TEC	San Diego, CA
H.C. Heller	FORD MOTOR COMPANY	Dearborn, MI
Dr. Liu	HYDRANAUTICS	Laurel, MD
Linda Schmauss	IONICS	Watertown, MA
J.N. Ryerson	LANCY INTERNATIONAL	Oceanport, NJ
Richard Baker	MEMBRANE TECHNOLOGY AND RESEARCH	San Francisco, CA
Jacob Shorr	MEMTEK	Woburn, MA
Sheryl Gainer	MILLIPORE	Bedford, MA
C.R. Blodgett	NATICK R&D CENTER.	Natick, MA

TABLE 2 - continued

LIST OF TOP PRIORITY CONTACTS

A. Membrane Technology

J.C. Hoffsommer	NAVAL SURFACE WEAPONS CENTER	White Oak, MD
Dean Spatz	OSMONICS	Minnetonka, MN
Dr. Chaim Katz	PALL TRINITY	Glen Cove, NY
Dr. Lee	RAI RESEARCH	Hauppauge, NY
George Schore	RAI RESEARCH	Hauppauge, NY
Barry Breslau	ROMICON	Woburn, MA
Mike A. Kozak	SUNFLOWER AAP	Lawrence, KA
D. Bhattacharyya	UNIVERSITY OF KENTUCKY	Lexington, KY

B. Ion Exchange Resins Technology

1. Companies

Name	Address
Eco-Tec LTD	Pickering, Canada
HPD, Inc.	Philadelphia, PA
Rohm and Haas	Philadelphia, PA
Permutit Co.	Paramus, NJ
Sybron Corp.	Birmingham, NJ
Graver Chemical	Union, NJ
Penfield, Inc.	Plainsville, CT
Dow Corning Corp.	Midland, MI
Omni Div., Ajax	Great Meadows, NJ
Floor Products Corp.	Great Meadows, NJ

TABLE 2 - continued

LIST OF TOP PRIORITY CONTACTS

B. Ion Exchange Resin Technology

2. Individuals

Name	Company	Location
Dr. Robert Kunin	CONSULTANT	Wayne, PA
Dr. Calvin Calmon	CONSULTANT	Princeton, NJ
James Szachta	ABERDEEN PROVING GROUND	Aberdeen, MD
Dr. John Hoffsommer	NAVAL SURFACE WEAPONS CENTER	Silver Spring, MD
Dr. Don Cary	US. EPA	Washington, DC
Frank McGarvey	SYBRON, CORP.	Birmingham, NJ
John Norden	MASON & HANGER	Louisville, KY
George Anspach	ATLANTIC RESEARCH CORP.	Alexandria, VA
Leonard Smith	ARMY AMMUNITION PLANT	Redford, VA
Jeff Codore	ENSIGN BICKFORD	Simsbury, CT
Richard Smith	WATER DESALINATION REPORT	Tracy's Landing, MD

Evaluation

Information was compiled to give an over-all history and general picture of the state of the art of different types of membranes and adsorptive resin technologies. Individual products were evaluated with relationship to treatment of hazardous wastes in the metals finishing or munitions industry according to the following criteria:

- Type
- Innovation or technique used to overcome inherent problems
- Demonstration status
- Economic considerations.

Recommendations were made on the feasability of using a particular technology in treatment of hazardous wastes in metals finishing or munitions industries. These recommendations are based on information supplied by manufacturers and researchers which cannot be verified within the scope of this project.

INFORMATION EXCHANGE

A Technical Information Exchange was held on September 21, 1984 in Columbia Maryland. Selected experts were invited to participate and deliver remarks about treatment of hazardous metals finishing and munitions wastes using "ion exchange" and membrane technologies. A proceedings containing abstracts and papers received was prepared and sent to EPA in a separate submittal. A video tape was made of the Information Exchange and was sent to EPA in a separate submittal.

SECTION V

RESULTS AND DISCUSSIONS

RESULTS OF INVESTIGATION

The results of investigation of metal finishing and munitions manufacture waste treatment indicate the need for additional research into the economics and material science of membrane technology. The electroplating and metal finishing industry as well as the munitions industry were surveyed for the applications of resins and membranes. The experiences of these industries with ion exchange and membrane technologies are discussed in this section.

TOXIC AND HAZARDOUS WASTES IN THE ELECTROPLATING AND METAL FINISHING INDUSTRY

According to estimation, the metal finishing industry utilizes more than one hundred surface finishing and fabricating processes that require aqueous applications and removals of various metals to and from metallic and plastic parts. An examination of the electroplating industry results in a list of species of interest (Table 3) which include the cationic metals involved in various types of electroplating, the manufacture of vehicles, the manufacture of printed circuit boards, and other finishing of industrial metals. Table 3 lists some common cations with their various oxidation states and associated anions. In most electroplating operations, various organic compounds as well as chelates are used to clean and brighten the metal. Although some known simple additives are EDTA, formaldehyde, and saccharin, the identities of organic compounds used in electroplating operations are often considered proprietary information.

The major problem, however, with the toxic and hazardous wastes from metal finishing is the chemical and physical environment which these species are found. Metals finishing uses extremes of pH values from 0 to 14. Often the baths are operated at high temperatures. Mixing of wastes occurs in the rinse phase. The organic chemicals may react and form unknown polymeric compounds in this harsh environment.[2]

However, the consensus of the membrane industry experts interviewed is that there is economic incentive to recover heavy metals. As the cost of the metals increases, platers find recovery more economical than disposal of hazardous sludges. The consensus of the membrane industry experts interviewed is that most metals finishers are small businesses and, therefore, cannot afford large capital investment in waste treatment and disposal.

TABLE 3

POTENTIAL POLLUTANTS IN

METAL FINISHING WASTES

CATIONS (Valence)	ANIONS (Valence)	OTHER MATERIALS
Cr (+3 +6)	Cr_2O_7 (-2)	Detergents
Cu (+1 +2)	CN (-1)	Brighteners
Ni (+2 +3)	SO_4 (-2)	Cleaners
Sn (+2 +4)	BF_4 (-1)	Chelates
Pb (+2 +4)	Cl (-1)	
Au (+1 +3)	S_2O_8 (-2)	
Ag (+1)	P_2O_7 (-4)	
Zn (+2)		
NH_4 (+1)		
Cd (+2)		

Although electroplating was the major area of concentration in this study, it also noted other areas of the metals finishing industry that had similar problems and possible solutions. The interest in cleanup of electroplating wastes results from the following causes:

- The Clean Water Act, which restricts the levels of toxic materials in wastewaters from metal finishing plants
- There are valuable metals available in the sludges and wastes that present an economic reason for recovery
- Reuse of the water
- The EPA's Office of Drinking Water is currently reviewing U.S. Public Health Service Standards on metals in water and it is probable the standards will be tightened.

There are two major sources of wastewater in the electroplating industry. One is the spent plating bath or the anodizing bath. The other major source is the rinse water. As these waste streams may be quite varied in composition, examples of these wastes are listed in Table 4.[3]

A brief discussion of effluent regulations and drinking water standards will be presented here, since these are the source of the numbers that have to be met by wastewater treatment. The discussion will come primarily from Gold's review of this subject.[4] The U.S. EPA effluent guidelines on pollutants discharged into publicly owned treatment works by electroplating plants prohibit those that interfere with, pass through, or are otherwise incompatible with the operation of publicly owned treatment works.[5] Plants with wastewater flows of less that 10,000 gallons per day must meet a less stringent level of control than do plants with greater flows. These smaller plants have limitations on cyanide, hexavalent chromium, lead, and cadmium. For the larger plants (in addition to cyanide) the concentrations of some or all of the following metals have been limited: lead, cadmium, copper, nickel, total chromium, hexavalent chromium, zinc, and silver. In addition, the sum of the individual concentrations of copper, nickel, chrome, and zinc (total metals) is limited. Dilution of the discharge streams is not acceptable as an adequate treatment to achieve compliance with the regulations. A list of the toxic pollutants and the concentration limitations is shown in Table 5. The maximum metals concentrations that can be tolerated in drinking water are also shown in the Table 5.[6]

TOXIC AND HAZARDOUS WASTES IN THE MUNITIONS INDUSTRY

There are unique and unusual hazardous waste problems in the munitions industry. The list of possible hazardous materials developed in the early phases of this project included many explosives used in both military and non-military purposes. Explosives commonly contain nitro groups (NO_2) attached to a wide variety of chemical structures, including benzene rings, and heterocyclic or aliphatic compounds. TNT is an example of a benzene ring (aromatic) compound, while such explosives as RDX, HMX and TAX are heterocyclic compounds. PETN is an aliphatic nitro compound. The full names of these and other compounds are listed in Table 6. While this list

is not exhaustive, it is indicative of compounds currently used in the munitions industry.

Organic or inorganic salts of lead and mercury are frequently used as initiators or primers of the explosion process. Some of these common primers are also listed in Table 6. Primers are extremely sensitive to heat, shock and friction.

The military munitions industry has a unique problem with "pinkwater." This is the effluent from LAP (Load, assembly and pack) plants, where artillery shells are cleaned and repacked with fresh explosives. Steam is used throughout this operation, generating "pinkwater," which is high in dissolved organics such as TNT, RDX, and HMX. This aqueous solution must be treated before discharge to the environment. The munitions industry is unique in the amount of nitrated organic compounds used and the inherent problems associated with them.

TABLE 4

TYPICAL COMPOSITIONS OF VARIOUS METAL TREATING WASTEWATERS

Source of Wastewater	CrO_3	Fe_2O_3	CuO	Al_2O_3	TDS	pH
	(grams per liter)					
Chrome Plating Bath	400	28.6	25	---	500	0.1
Copper Stripping Bath	200	---	---	---	300	0.7
Aluminum Anodizing Bath	100	---	---	17	150	0.8

Source of Wastewater	CrO_3	Fe_2O_3	CuO	Al_2O_3	TDS	pH
	(parts per million, ppm)					
Chrome Rinse Water	50	3	---	---	300	2.5
Anodizing Rinse Water	25	---	---	---	300	3.0
Coolant Water Blowdown	50	---	---	---	1000	7.5
Mixed Plating Rinse Water	10	2	25	1	600	2.5

Source: Kunin, R. Ion Exchange for Metal Products Finisher. Products Finishing, April, May, June, 1935.

TABLE 5

PROPOSED EPA STANDARDS (mg/l)

Substances	Electroplating Process Wastewaters				National Primary Drinking Water Regulations
	Discharge ≤0.01 MGD		Discharge >0.01 MGD		
	30 day avg	Max/day	30 day avg	Max/day	Max. Concentration
Arsenic	---	---	---	---	0.05
Barium	---	---	---	---	1.0
Cadmium	0.05	1.00	0.50	1.00	0.01
Chromium (Cr^{+6})	0.09	0.25	0.09	0.25	0.05
Cyanide (free)	0.80	2.00	0.08	0.20	---
Cyanide (total)	0.24	0.64	---	---	---
Lead	0.40	0.80	0.40	0.80	0.05
Mercury	---	---	---	---	0.002
Nitrate (as N)	---	---	---	---	10.0
pH (pH units)	---	---	---	7.5 to 10.0	---
Selenium	---	---	---	---	0.01
Silver	---	---	---	---	0.05
Total Suspended Solids	---	---	10.00	15.00	---

Materials Requiring Treatment

Materials such as nitroso- and nitro-substituted organic compounds have been known for some time to be present as contaminants in the effluent waters from munitions manufacturing and disposal facilities. Those compounds constitute a potential environmental hazard because the contaminated effluents may infiltrate ground water, streams, or rivers from which drinking water is obtained and are more difficult to treat.

TNT (2,4,6-trinitrotoluene) is probably the major chemical that is in the U.S.A. exclusively in government owned facilities. The production rate varies, depending on the nature of defense requirements. Water pollution from the manufacture of TNT may arise in three ways:[7,8]

- Washing of the solid or molten TNT with 16% aqueous sodium sulfate selectively removes the 3-5% of TNT isomers containing a nitro group in the three or five position. The intensely colored high-solids spent wash solutions are known as "red waters." In a modern plant, these solutions may contain about 25% dissolved solids, including 9% organics, with the rest being sodium sulfite, sodium nitrate, and sodium nitrite. The present method of disposal of these "red waters" is to concentrate them either for use as additives in the paper industry or else for incineration.

- Washing of the partially purified TNT following the sodium sulfite (or "selite") treatment produces "pinkwater." "Pinkwater" may also be produced as a result of building washdown, scrubber blowdowns, and a variety of other sources such as bomb and shell washings which, when carried in streams at neutral to alkaline pH and exposed to sunlight, form colored organic complexes that gave the water its pink appearance.

- Wash waters from the TNT finishing process have 2,4-DNT as well as TNT as their principal pollutants along with other color-producing compounds. When these wastewaters are exposed to sunlight at concentrations of about 1 mg/l or greater, a pink to amber color results.

The need to remove the colored compounds from munitions plant waste effluents arises from requirements under the Clean Water Act and the Safe Drinking Water Act. The compounds causing the color may be toxic in sufficient quantities. For example, it has been stated that TNT at concentrations of 2.5 ppm is toxic to fish and other aquatic life.[8]

TABLE 6

MATERIALS POTENTIALLY PRESENT IN

HAZARDOUS WASTES FROM ARMY MUNITIONS

RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine)

HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)

TNT (Trinitrotoluene)

DNT (Dinitrotoluene)

NT (Nitrotoluene)

TAX (1-Acetyl-1,2,3,4,5,6-hexahydro-3,5-dinitro-1,3,5 triazine)

SEX (1-Acetyl-1,2,3,4,5,6,7,8-octahydro-3,5,7-trinitro-1,3,5, 7-tetrazocine)

PETN (Pentaerythritol tetranitrate)

Tetryl (N-Methyl-N,2,4,6-tetranitrobenzenamine)

Nitroglycerin

Nitrocellulose

Nitroguanidine

PRIMERS

Lead Styphnate Pb ($C_6HN_3O_8$)

Lead Azide N_6Pb

Mercury compounds

There are a number of other undesirable and dangerous compounds that may be found in the production of explosives and propellants. One example is styphnic acid, which is present in plant effluents resulting from the manufacture of lead styphnate. Styphnic acid may create an explosive hazard. Unfortunately, commonly accepted techniques for chemically destroying the acid, either through oxidation or reduction, may cause formation of toxic reaction products as well as residues of the toxic reagents that were added in some cases. For example, in the oxidation process, the addition of chlorine, either as hypochlorite or through electrolysis, may result in the formation of the strong lachrymator chloropicrin.[9,10]

Heck[1] has presented a table (Table 7) of the NPDES allowable discharges of various contaminants at different Army Ammunition Plants (AAP). Table 8 shows the composition of industrial wastewaters that must be reduced to the levels shown in Table 7.

USE OF RESIN SYSTEMS

Information on new ion-selective resin technologies for treatment of electroplating and munitions toxic and hazardous wastes was considered for this study. The phrase "ion-selective resin technologies" should be discussed in order to properly identify the materials that have been considered.

Conventional ion exchange resins may be regarded as three dimensional bead structures to which an exchangeable ion has been attached. The most common currently used resins have polystyrene crosslinked by varying amounts of divinylbenzene (DVB) as the insoluble polymer matrix. There are other such structures, however, that are less commonly used. For example, the first synthetic ion exchangers were based on the phenol-formaldehyde reaction. In some of the commercially available resins today, the polymer matrix consists of methacrylic or acrylic acid crosslinked with DVB or the condensation product of epichlorohydrin with anions. A number of other types of polymer matrices that have been developed for specific ion removal will be described.

The inert polymeric matrices named above are then made acidic or basic so that they can remove cations or anions from solution. In the case of cation exchange resins, groups such as SO_3^- or COO^- are attached to the crosslinked polymer matrix. Phenolic or phosphonic groups are also used. The result is a variation in the nature of the fixed anion. Since it is desirable to be able to use the resins over as wide a pH range as possible, the sulfonic resins are most commonly used. The sulfonic acid group will be dissociated even at very low pH values, thus making exchange possible. The exchange versus pH properties of the other acidic groups are a function of their dissociation constants, so that the phosphonic resins can be used at a pH greater than 3, the carboxylics near the neutral pH and the phenolics only at higher (very alkaline) pH.

TABLE 7

EXISTING NPDES PERMIT DATA[10]

Location	Contaminant	Allowable Discharge Av. (mg/l)	Max. (mg/l)
Iowa AAP	TNT	0.5	1.0
	RDX	15.0	25.0
Joliet AAP	TNT	0.5	0.75
Radford AAP	TNT	0.5	0.75
Volunteer AAP	TNT	0.3	0.50
Milan AAP	TNT	---	1.0
Milan AAP	RDX	---	1.0

Source: USA Pat. NO. 2,487,627. Process for the Decomposition of Styphnic Acid. November 8, 1949.

TABLE 8

BASIC CHARACTERISTICS OF INDUSTRIAL WASTEWATERS

FROM MUNITION FACILITIES[11]

Parameter	Locations		
	A	B	C
Flowrate (gpd)	20,000	100,000	1,000,000
Temperature (^{o}F)	60 - 140	160	Ambient
pH	7	7	3.5
TNT (mg/1)	100 - 250	150 - 400	0 - 50

If a cation exchange resin in the hydrogen form is placed in equilibrium with a sodium salt, e.g. NaCl, the following reaction will take place:

$$RSO_3^- H^+ + Na^+ Cl^- \longleftrightarrow RSO_3^- Na^+ + H^+ Cl^-$$

$$RCOO^- H^+ + Na^+ Cl^- \longleftrightarrow RCOO^- Na^+ + H^+ Cl^-$$

Where R is the fixed polymeric groups, SC_3 or COO^- are the attached anionic charges, and H^+ is the exchangeable ion.

By placing resin beads (in the H^+ form) in a column and passing the liquid waste through that column, a series of exchange equilibria are produced that ultimately result in the complete removal of Na^+ from the solutions. The resin in the column may have any desired cation attached and then exchanged for other cation(s) in the solution that flows through the bed.

Cation exchange resins show selectivity for certain ions over others. Generally, the higher the valence state of the cation, the greater is selectivity of the resin for it. This is explained by analogy to the solubility of the sulfonic salts. For cations for the same valence state, the smaller hydrated ion is generally adsorbed preferentially, since the resin does not have to swell as much to accommodate it. This selectivity tends to be lowest at low crosslinking with DVB, and highest a high DVB content-a direct function of the ability of the hydrated ion to penetrate the resin matrix. Anion exchange resins generally take the form of weak base resins (RNH_2), (R_2NH), (R_3N), or strong base resins (R_4NCL). The weak base resins function as if they were acid adsorbents, e.g.,

$$RNH_2 + HCL \longleftrightarrow RNH_2\ HCL$$

since the RNH_2 group is not disassociated, whereas the strong base resin exhibits true ion exchange:

$$R_4N^+OH^- + Na^+\ Cl \longleftrightarrow R_4N^+\ Cl^- + NaOH$$

This ion exchange ability of strong acid and base resins makes them useful for systems such as plating solutions, where materials to be removed are ionic in nature.

Unfortunately, many of the more toxic materials that need to be removed from waste solutions, especially those in wastes from munitions, tend to be relatively nonionic in nature. The result is that this removal must follow an adsorption mechanism, making materials like activated carbon more useful for that purpose. In order to make ion exchange resins more suitable for adsorption of large nonionic molecules, Rohm and Haas developed a new type of resin in 1959.[12] Previous polystyrene-divinylbenzene ion exchange resins had been crosslinked to form a "gel" matrix structure that had specific pore sizes depending upon the amount of DVB present. The pore size, coupled with the ionic nature of the exchange group, limited the ability of large nonpolar molecules to enter the resin structure and be adsorbed on the solid walls by weak Van der Waals' forces. The new resin bead structure is called macroreticular and differs from the gel resins in that the macroreticular resin bead has the appearance, under high magnification, of compacted gel

microspheres. This porous structure is created by polymerizing the styrene and DVB in the presence of a third ingredient, in which the monomers are soluble but the resultant polymer is insoluble. The third ingredient is then removed from the resin structure leaving a resin bead that has both a continuous resin phase and a continuous pore phase, resulting in considerable internal surface area. The unique fixed porosity of the macroreticular structure (as compared to a gel structure) means that the surface exchange sites are available even in nonaqueous media where there is no water for the hydration or swelling necessary in gel resins. The effective resin surface in contact with the fluid to be processed is increased to many times that of a gel resin.[2]

Rohm and Haas has proceeded further in this direction through the development of macroreticular polymeric adsorbent resins. In the manufacture of these resins, control of pore size, porosity and surface area, together with modification or change of the polymer chemistry, allows tailoring of the adsorbent to a wide range of adsorption applications.[2] It creates a resin which is no longer a true "ion-exchange" resin, but rather an adsorbent that, in some cases, starts to approach the capacity of activated carbon. Macroreticular adsorbents have become available with either aromatic character, derived from the incorporation of styrenic monomers, or aliphatic character resulting from the the use of acrylic monomers in their synthesis. These latter copolymers yield a more polar surface with hydrophilic characteristics. Modifying the resin structure by incorporating monomers of varying clarity allows production of adsorbents with a wide range of hydrophilic characteristics. Regeneration or elution of materials adsorbed onto these synthetic resins can be accomplished by solvent treatment, changing ionic concentrations, acid or base addition, or thermal elution.

Some of the same properties of ion exchange resins that influence reactions in aqueous media also affect reactions in non-aqueous media. The primary difference is availability of exchange sites on the resins. In aqueous media, the resin is fully hydrated and expanded to the maximum degree the crosslinkage will permit. In non-aqueous media, the solvent action of the media on the resin usually causes less swelling, thereby reducing the availability of exchange sites for reactions. It follows that the more polar a solvent (higher dielectric constant), the more favorable the rate of exchange. Other factors (such as molecular weight, ionic size and temperature) will influence rate of exchange and capacity similar to that of aqueous media.[2,3]

Macroreticular resins, with their fixed porosity in the resin matrix, are usually more efficient in non-aqueous applications. The continuous pore phases of these resins allows non-aqueous phases to fill them, thereby gaining access to the exchange sites which exist on the internal surfaces of the resin beads. The diffusion path length into the gel phase is substantially shortened with these resins, thus reducing their dependency upon gel phase swelling as compared to gel resins.

In applications in which the medium is not water soluble, regeneration of macroreticular ion exchange resins is generally accomplished by using an intermediate solvent such as alcohol (or one miscible with both the solvent and water). This is done so that an aqueous regeneration system can be used to regenerate the resin with appropriate acid or base. The displacement of the water used in the regeneration and rinsing step can then be carried out

with the intermediate solvent, which in turn would be displaced by the solvent or non-aqueous media to be used.[13]

The result of all this activity is that materials starting out as ion exchange resins with a small amount of adsorptive capacity now are at one end of a spectrum of resin types. The other end of the spectrum consists of resins that have high adsorptive capacities and little or no ion-exchange properties. Indeed, technically the term "ion-exchange" should be dropped from their names.

For the purposes of this report, we will continue to use the term "ion-exchange resins" for the entire gamut of resins used in the industries that we are studying. As the reader will see, the true "ion exchange" resins tend to be of most use in handling wastes from the electroplating industry, while the adsorption types are much more useful in the munitions industry. Table 9 shows properties typical of commonly used ion exchange resins.

The selectivity of resins for some ions over others has been mentioned. It is usually expressed as the Selectivity coefficient, K_B^A, which is defined for the exchange reaction of ions A and B:

$$RSO_3^- A^+ + B^+ \text{ ----------> } RSO_3^- B^+ + A^+$$

where K_B^A is the derived by comparing the amounts of B^+ and A^+ in the resin with those in solution. Kunin[3] has presented typical selectivity coefficients for strong acid and base ion exchange resins in Table 10.

Obviously, when a solution containing ion B^+ is passed through a bed of resin in the A^+ form, all of the B^+ will be removed by the resin and replaced by A^+ until the column is "saturated", or else the flow is such that leakage occurs before that time. In practice, the latter is what happens and B^+ begins to appear in the column effluent at a time and concentration level that is a function of such things as selectivity, bed height, flow rate, turbulence, effectiveness of the previous bed regenerations, etc. Using resin beds, ions can be selectively removed from solution as shown in Table 11.[14]

A number of other resins are specific for various ions. This particularly includes "chelating resins," i.e., those in which the functional group is basically that of a chelate specific for certain ions. Calmon[15] has prepared a table (Table 12) showing specific exchangers or groups that will adsorb metals selectively.

Commercially available macroreticular chelating resins include Amberlite Ionac SR-1 and Ionac SR-11. These resins are most sensitive to selective metal removed at low pH values. Thus, Table 13, taken from Waity[16], shows the selectivity of Amberlite IRC-718 for metal ions at a pH of four.

At a pH of nine, the selectivity for all these metals relative to calcium drops very sharply, except for cobalt. The cobalt selectivity goes up from 6.7 at pH 4.0 to 8.3 at pH 9.0.

Chelating resins are also used in Japan[17] and Germany[18] for recovery of heavy metals from wastewater. For the commercially available Ionac styrene-DVB copolymer using iminodiacetic acid as the functional group, McGarvey and Ungar[19] have presented the following selectivity series:

$$Cu^{+} >> Fe^{+2} > Ni^{+2} > Co^{+2} > Pb^{+2} > Mn >> Ca^{+2} >> Mg^{+2} >> Na^{+}$$

$$Hg > Cu > Pb > Ni > Cd > Zn > Co > Mn > Ca > Mg > Ba > Sr >>> Na.$$

McGarvey and Ungar[19] also state that chelating resins prepared with sulfur as part of the complex bind gold and platinum metals very selectively from acid solutions. A macroporous chelating resin, Ionac SR-3, is highly selective for precious metals such as gold and others of the platinum group from acid solutions. The redox reaction capability of these resins then can lead to the formation of metallic gold. They also state that weak ester groups, CO_2 R can be used in resinous structures to adsorb gold, probably through hydrolysis of the group.

Another interesting commercially available resin type is the Amborane family of reductive resins. The resins contain amine-borane reducing groups and are comparable to monomeric amine-boranes but offer greater stability, selectivity and process advantages for precious metal recovery. The advantage of these resins is that they combine very high capacity with excellent selectivity for precious metals in the presence of base metals.

These resins remove the ionic metal from solution by reduction, concentrating the reduced metal within the highly porous bead. Amborane 345 is derived from acrylic polymer while Amborane 355 is based on crosslinked styrene. The metals that can be recovered with these resins are shown in Table 14. To recover the metal values, the reductive resin is slowly roasted at 500°C to 800°C in a well ventilated area.

Finally, the development of the Graver precoat technology, which combines filtration, ion exchange, and adsorption should be mentioned.[20] In this approach, powdered ion exchangers are used non-regenerably as a disposable precoat filter. It is claimed that a fraction of an inch of precoat layer can be as effective as several feet of granular adsorbent beads.

USE OF MEMBRANE SYSTEMS

Membrane technology for industrial purposes has been commercially possible for the last 30 to 40 years. Traditionally, a membrane was defined as a thin pliable sheet or layer that allowed one component of a solution to pass through while preventing other components from passing through. As knowledge increases, the definition is being broadened. This report used Strathmann's definition:[21] "A membrane is an interphase which separates two phases and restricts the transport of various chemical species in a rather specific manner."

TABLE 9

PROPERTIES OF ION EXCHANGE RESINS[3]

Chemical Structure	Physical Structure	Ion Exchange Moisture Content %	Capacity meq./ml.
Cation Exchange Resins			
Sulfonic	Microreticular	46	1.9
Sulfonic	Macroreticular	49	1.8
Carboxylic	Macroreticular	48	3.5
Anion Exchange			
Quaternary	Microreticular	45	1.4
Quaternary	Macroreticular	62	1.0
Tertiary Amine	Macroreticular	50	1.4

SOURCE: Kunin, R. Ion Exchange for the Metal Products Finisher. Products Finishing, April, May, June 1935.

TABLE 10

APPROXIMATE ION EXCHANGE SELECTIVITY COEFFICIENTS

	Ion A	Ion B	Coefficient, K_B^A, at 50% Saturation
Cation Exchanger (Amberlite IR-120)	H^+	Li^+	0.8
	H^+	Na^+	2.0
	H^+	K^+	3
	H^+	NH_4^+	3
	H^+	Ag^+	18
	H^+	Tl^+	24
	Na^+	K^+	1.8
	H^+	Ca^{+2}	42
	Ni^{+2}	Ca^{+2}	2.5
Anion Exchanger (Amberlite IRA-400)			
	Cl^-	F^-	0.1
	Cl^-	Br^-	2.5
	Cl^-	I^-	18
	Cl^-	NO_3^-	3
	Cl^-	OH^-	0.5
	ClO_4^-	SCN^-	0.6

SOURCE: Kunin, R. Ion Exchange for the Metal Products Finisher. Products Finishing, April, May, June 1935.

TABLE 11

GUIDE TO SELECTIVE SORPTION OF METALS BY ION-EXCHANGE RESINS[14]

Metal (form)	Resin	Resin form	Influent pH
Antimony (antimonite)	SB	Chloride	1-14
Antimony (antimonite)	WB	Free base	4-10
Arsenic (arsenate, arsenite)	SB	Chloride	1-14
Arsenic (arsenate, arsenite)	WB	Free base	4-10
Barium (Ba^{+2})	WA	Sodium, hydrogen	1-8
Cadmium (Cd^{+2})	WA	Hydrogen	3-8
Cadmium (anionic complex)	WB,SB	Free base, chloride	6-12
Cesium (Cs^{+})	WA	Sodium	7-14
Chromium (Cr^{+3})	SA	Hydrogen	0-5
Chromium (chromate)	SB,WB	Sulfate chloride	0-14
Cobalt (Co^{+2})	SA	Ammonium	1-8
Cobalt (Co^{+2})	WA	Sodium hydrogen	5-9
Cobalt (Co^{+2})	WB	Free base, sulfate	4-10
Cobalt (anionic complex)	SB	Chloride	strong acid
Copper (Cu^{+2})	WA	Hydrogen sodium	5-8
Copper (Cu^{+2})	WB	Free base, sulfate	3-10
Gold (anionic complex)	SB	Hydroride	0-14
Iron ($FeCl_4^{-}$)	SB	Chloride	2-12 M HCl
Iron (organic chelate)	WB	Free base	3-8
Lead (Pb^{+2})	WB	Free base, sulfate	4-6

TABLE 11 (continued)

GUIDE TO SELECTIVE SORPTION OF METAL BY ION-EXCHANGE RESINS[14]

Metal (form)	Resin	Resin form	Influent pH
Lead (chloride complex)	SB	Chloride	0-14
Mercury	WB	Free base	5-14
Mercury (chloride complex)	SB	Chloride	0-14
Molybdenum (molybdate)	WB	Free base, sulfate	3-9
Nickel (Ni^{+2})	WA	Sodium, ammonium	5-9
Nickel (Ni^{+2})	WB	Free base, sulfate	4-7
Platinum (anionic complex)	SB	Chloride	0-14
Rhenium (anionic complex)	SB,WB	Chloride, free base	0-14
Selenium (selenite)	WB	Free base	2-6
Silver (Ag^{+})	SA	Hydrogen, sodium	0-7
Silver (Ag^{+})	WB	Free base	5-9
Silver (anionic complex)	SB,WB	Chloride, free base	0-14
Tungsten (tungstate)	SB,WB	Chloride, free base	0-14
Vanadium (vanadate)	WB	Free base, sulfate	2-8
Zinc (Zn^{+2})	WA	Sodium	5-10
Zinc (Zn^{+2})	WB	Free base, Sodium	4-7
Zinc (Zn^{+2})	SA	Hydrogen	0-7

Note: WB=Weak-base anion exchanger, SB=Strong-base anion exchanger. WA=Weak-acid cation exchanger. SA=Strong-acid cation exchanger. FB=Free base.

TABLE 12

SPECIFIC GROUPS CONTAINING EXCHANGERS FOR SPECIFIC IONS[98]

Ion	Specific Exchanger or Group
Ammonium	Clinoptilolite (Baroid-Division of NL)
Arsenic	Flourone
Beryllium	Diallyl phosphate
Bismuth	Pyrogallol
Boron	N-methylglucamine (Rohm and Haas Amberlite XE-243)
Calcium	Gallic acid, iminodiacetic acid, and diallyl phosphate
Cesium	Methylene sulfonic acid (Bayer-Lewatit DN and Shamrock Duolite C-3)
Cobalt	8-hydroxyquinoline Beta-diketone Ethylenediaminetetraacetic acid

TABLE 12 (continued)

SPECIFIC GROUPS CONTAINING EXCHANGERS FOR SPECIFIC IONS[98]

Ion	Specific Exchangers or Group
Copper	Diphenylthiourea 8-hydroxyquinoline Anthranilic acid Beta-diketone Ethylenediaminetetraacetic acid
Cyanide	Anion exchanger (Rohm and Haas Amberlite XE-275 for ferrocyanide)
Germanium	Flourone Polyhydric phenols
Gold	Polyisothiouronium (Ayalon SRAFION-NMRR)
Iron	Alginic acid Diallyl phosphate Hydroxamic acid M-phenylglycine Thiol (AKZO Chemical Co.) Anthranilic acid
Lead	Pyrogallol (AKZO Chemical Co.-IMAC T-73)
Magnesium	Alginic acid Phenyldiaminoacetic acid
Mercury	Thiol (AKZO Chemical Co-Imac TMR; Diamond Shamrock Duolite ES464) Polyisothiouronium (Ayalon SRAFION-NMRR) Pyrogallol Dithiocarbamate (Nippon Soda-NISSO Alm)
Nickel	Dimethylglyoxime Thiol (AKZO Chemical Co.) 8-hydroxyquinoline

TABLE 12 (continued)

SPECIFIC GROUPS CONTAINING EXCHANGERS FOR SPECIFIC IONS[98]

Ion	Specific Exchangers or Group
Nickel (cont.)	Beta-diketone Ehthylenediaminetetraacetic acid
Nitrate	Alkylated amidines
Palladium	Aminophenol and nitro groups Guanidine
Platinum	Polyisothiouronium (Ayalon SRAFION-NMRR) Guanidine Polyisothiouronium (Ayalon SRAFION-NMRR)
Potassium	Dipicrylamine
Silver	Thiol Amino-carboxylic
Strontium	Diallyl phosphate
Thorium	Arsenic acid
Titanium	Chromotropic acid
Uranyl oxide	Schiff base-dinitrophenol
Zinc	Anthranilic acid Phosphonic acid resin
Zirconium	Phosphonic

SOURCE: Petrov, V.F., Lebedeva, B., Chikin, Y., Balakin, V.M., and Vydrin, A.; Zh. Prikl.. Khim.

TABLE 13

SELECTIVITIES OF AMBERLITE IRC-718 FOR METAL IONS

pH = 4.0

Metal Ion	K_M
Hg^{+2}	2800
Cu^{+2}	2300
Pb^{+2}	1200
Ni^{+2}	57
Zn^{+2}	17
Cd^{+2}	15
Co^{+2}	6.7
Fe^{+2}	4.0
Mn^{+2}	1.2
Ca^{+2}	1.0

TABLE 14

AMINE-BORANE RESIN SELECTIVITY FOR METAL-ION SPECIES

Reactive		Non-reactive	
Metal Ion	Source	Metal Ion	Source
Au^{+3}	$AuCl_4^-$	Group 1A*	Chloride salts
Pt^{+2}	$PtCl_4^-$	Group 11A*	Chloride salts
Pt^{+4}	$PtCl_6^-$	Group 111A*	Chloride salts
Pd^{+2}	$PdCl_2$	Group 1VA*	Oxides and nitrates
Ag^{+1}	$AgNO_3$	Cr^{+3}	$CrCl_3$
Ir^{+3}	$IrCl_3$	Mn^{+2}	$MnCl_2$
Rh^{+3}	$RhCl_3$	Fe^{+2}	$FeCl_2$
Hg^{+1}	Hg_2Cl_2	Fe^{+3}	$FeCl_3$
Hg^{+2}	$HgCl_2$	Co^{+2}	$CoCl_2$
CH_2Hg^{+1}	CH_3HgCl	Ni^{+2}	$NiCl_2$
As^{+3}	As_2O_3	Cu^{+1}	CuCl

TABLE 14 (Continued)

AMINE-BORANE RESIN SELECTIVITY FOR METAL-ION SPECIES

Reactive		Non-reactive	
Metal Ion	Source	Metal Ion	Source
Sb^{+3}	Sb_2O_3	Cu^{+2}	$CuCl_2$
Bi^{+3}	$Bi(NO_3)_3$	Zn^{+2}	$ZnCl_2$
		Cd^{+2}	$CdCl_2$
		Ru^{+3}	$RuCl_3$
		Sn^{+4}	$SnCl_4$
		Pb^{+2}	$Pb(NO_3)_2$
		Tl^{+3}	$Tl_2(SO_4)_3$

*Periodic table of the elements.

Membranes technology is currently used or being developed for use in the following industrial categories:

- Medicine
- Pharmaceuticals
- Water conservation
- Food and dairy
- Gas separations
- Paper industry.

Three problems are associated with membranes that have prevented their wider use in the industrial markets. They are:

- Low flux through membranes
- Fouling and adsorption on membrane skin lowers the flux
- Low resistance to harsh chemical environments such as very high or very low pH and to high temperatures.

New applications have been made possible by advances in the area of membrane research:

- New polymers and novel membrane materials can be operated over a broad pH and temperature range
- Fundamental understanding of transport across membranes
- Development of thin-film composite membranes with insignificant compaction problems.

DISCUSSION OF FINDINGS

A review of information sources presented the following topics concerning resins and membrane technology applied to plating and munitions wastes: adsorption by activated carbon, resin systems, annual costs, metal recovery, size exclusion membranes, liquid membranes, and demonstration status. Product applications are discussed but not recommended.

USE OF RESIN TECHNOLOGY TO TREAT TOXIC AND HAZARDOUS MUNITIONS WASTES

Adsorption on Activated Carbon

A number of approaches to reduce color from hazardous munitions wastes have been attempted. These include biodegradation processes,[8] changes in manufacturing procedures, improved housekeeping,[7] oxidation or reduction of styphnic acid,[9] evaporation ponds and open burning.[22] Activated carbon became the logical candidate adsorbent, has received the most study, and is the most effective material used to date in terms of adsorption capacity. Its major disadvantage is in the requirement for thermal regeneration which adds substantially to the process cost.

A 1959 study by Haines [11,23] showed the average saturation capacity of activated carbon column for TNT was 55% (0.55 pounds of TNT per pound of carbon.) The optimum flow-rate was 4-7 gpm per sq. ft. of surface area (gpm/sq. ft.). As a result of his study, several activated carbon treatment plants were installed at the Iowa Army Ammunition Plant in Burlington, Iowa and have successfully removed TNT induced red color for up to nearly 20 years.

Rosenblatt[7] was able to improve the capacity of activated carbon for TNT as a result of a detailed comparative study of available activated carbons. He concluded that activated carbons derived from bituminous coal were the most promising, (i.e., Calgon Filtrasorbs 300 and 400 and Westvaco WV-L, WV-W and WV-G). The following were excluded from further consideration: Westvaco Nuchar C-115; Kerr-McGee natural and synthetic bone char: Barnebey-Cheney JV wood charcoal; Barnebey-Cheney YF nutshell charcoal; Atlas Darco S51 lignite charcoal; and Atlas Darco KB sweetgum sawdust charcoal. Most of the charcoals studied had been manufactured in granular form and ground to powder for these experiments.

12-40 Mesh Filtrasorb 400 was picked as the carbon for detailed study since this was already being used at one U.S. installation. Rosenblatt's work showed that the saturation capacity of the column was 3.20 gram (i.e., 0.78 gram of TNT per gram of carbon) and compared favorably with the 0.55g/g figure reported by Haines.[23] In a considerable breakthrough, Rosenblatt was able to regenerate part of the original sorptive capacity of the activated carbon with warm toluene and reuse the carbon. The toluene solution contained 1.82 grams of TNT. In the second use cycle, only 1.51 grams (i.e., 0.37 gram of TNT per gram of carbon) was adsorbed. A second regeneration of the column with toluene removed 1.40 grams of the adsorbate. Thus, it appeared likely that the sorptive capacity of the carbon would approach some lower, but constant, level after repeated use.

The study by Kurz[9] on styphnic acid removal from nitric acid resulted in removal values stated in Table 15 for activated carbon, granular charcoal, and a strong base anion exchange resin.

Kurz also found that the presence of free nitric acid was necessary for an effective adsorption on carbon, since free styphnic acid, and not the styphnate ion was adsorbed. This finding was supported by the observation that addition of alkali to carbon powder containing adsorbed styphnic acid released styphnate (an ion) into the solution. The comparatively small amount of styphnic acid adsorbed on the ion exchange resin may also have

been caused by strong competition from nitrates which are present in a molar ratio of about 200 or 300 to one mole of styphnic acid. Had the nitrates been removed first, it is possible that more styphnic acid would have been adsorbed by the strong base anion exchanger.

Removal of Contaminants by Resin Systems

The use of Amberlite IRA-401 in the chloride form for the removal of styphnic acid from solution has been discussed above. In general, ion exchange resins are not very effective for the removal of hazardous waste contaminants from munitions waste water, since the materials whose removal is desired generally are non-ionic in nature and have a fairly large molecular size. An interesting study on the use of strong base resins for this purpose was carried out by Hoffsommer et al.[24] who studied removal of hydrolyzable non-aromatic nitroso- or nitro-substituted explosive compounds from water by adsorption on a strongly basic anion exchange resin in the OH- form. The explosive, adsorbed on the resin, is rendered harmless by decomposition into non-toxic materials. In one example, an aqueous solution containing 440 ppm of RDX was passed through a column of Amberlite IRA-410 resin, with the content of the RDX in the effluent being less than 0.04 ppm. In another example, an aqueous solution containing 167 ppm HMX was passed through a column of the Amberlite IRA-410, with the average HMX in the effluent being less than 0.01 ppm. In each case, the spent resin was regenerated with sodium chloride followed by sodium hydroxide. Materials removed were nitroamines, nitrosamines, nitrite esters and nitrate esters. Explosive materials that are claimed to be treatable by this method include RDX, HMX, pentaerythritol tetranitrate, nitroglycerin, ethylenedinitramine, nitrocellulose, pentaerythritol trinitrate, ethylene glycol dinitrate, glycerol monolactate trinitrate, and cyclotrimethylenetrinitrosamine.

The possible decomposition mechanisms of the explosives on the resins were not discussed, but may have been caused by the higher pH via hydrolysis during regeneration. Aromatic compounds appeared to adsorb on the resins but could not be removed. This lack of desorption may have been caused by formation of strong Meisenheimer complexes with the organic resin structure that defy regeneration. A cation exchange resin is reported to have been evaluated for the removal of lead from blasting cap operations, but without much success.[25]

Heck[11] has reported on one of the first studies made[26] (1959) on the investigation of some 34 different materials: 27 ion exchange resins, 3 resinous adsorbents, 3 activated carbons, and fullers earth for TNT adsorption. Activated carbon out-performed the ion exchange resins and was selected for the removal of TNT induced red color at the Iowa Army Ammunition Plant. The process has been successful for nearly 20 years. The result of these studies is that most of the work in the munitions industry has been with the use of macroreticular (adsorbent) resins and a discussion of their results follows. Some of the initial studies in this field were by Spano et al., [8] Schultz et al.,[27] and Layne and Tash.[26]

TABLE 15

STYPHNIC ACID REMAINING IN SOLUTION

AFTER ADDITION OF VARIOUS ADSORBENTS[7]

Adsorbent*	Styphnic Acid in Solution ppm
Activated Carbon "DARCO", Grade S51 "Atlas" Chem Ind.	1
Charcoal, granular, activated for gas adsorption, BDH	23
Charcoal, animal, granular for filters, BDH	575
Amberlite resin IRA-401(CL), Anal. Grade, Rohm & Haas	95

NOTE: *20 grams of adsorbent added to 1 liter of 0.5 N HNO_3 mixture containing 790 ppm of styphnic acid

SOURCE: Matsuba, T. Recovery of Heavy Metals from Wastewater with Chelating Resins. Kagaku Socki, 23 (10): 141-5, 98, 1981.

Spano has described work at the U.S. Army Natick Labs on the direct adsorption of TNT on polymeric resins. He used Amberlite XAD-2. Initially this resin was considered as a potential medium to concentrate the nitrobodies in the "pinkwater" for analytical purposes. However, results of preliminary experiments proved so promising that it was decided to investigate XAD-2 as a potential adsorbent bed to clean the total effluent stream from the TNT finishing process.

Spano's column studies show that running colorless wash waters from the TNT finishing house of an actual ammunition plant through an XAD-2 column resulted in an acidic eluant clean of TNT. Upon neutralization, this eluant did not develop the characteristic "pink-amber " color due to TNT. A comparison between columns of activated carbon (Filtrasorb 400) and the Amberlite XAD-2 showed that the two were comparable for influent throughputs equivalent to about 600 adsorbent bed volumes. The XAD-2 had the advantage of regenerability with acetone, whereas the Filtrasorb-400 did not. Specifically, the TNT recovered from the XAD-2 column with acetone was four times greater than that which could be recovered from the Filtrasorb-400. They recommended that the resin column be used to adsorb the major fraction of nitrobodies and color-producing constituents of a TNT stream, with an activated carbon bed being used for polishing purposes since the XAD-2 did allow some of the color components to pass through while the Filtrasorb-400 did not.

Smith[28] has worked with a macroreticular resin at Radford Arsenal for removal of explosives. The resin adsorption and the subsequent regeneration with acetone were considered by him to be effective but expensive.

Heck[11] presented a summary table, shown in Table 16. The Table combines the results of several different investigators[29,30,31] on laboratory, pilot, and full scale installations for activated carbon and Amberlite XAD-4.

Heck[10] further stated that XAD-4 compared favorably with activated carbon, even though the adsorption capacities are lower for economic reasons, since XAD-4 can be regenerated with acetone in contrast to the cost of regenerating activated carbon thermally. He states that regeneration and solvent recovery with acetone has been demonstrated at the pilot plant scale, including more than 99% acetone recovery. He also advocates a resin-carbon system, using the carbon as the polishing agent. Specifically, he suggests a system where wastewaters from the filter are piped to one of two resin columns which are in parallel; one is off stream while the other is on. The carbon column acts as a polishing column in case one of the resin columns experiences an abnormal breakthrough. Once a resin column reaches breakthrough, it is automatically taken off line and the wastewaters are directed to the other column. The saturated column is then backwashed with approximately six bed volumes of acetone, contaminated acetone is then distilled and condensed to 99% plus recovery. Estimated operating costs for 80 gpm carbon and resin-carbon systems are shown in Table 17.

TABLE 16

ADSORPTION CAPACITIES

Capacity Expressed As Pounds NB/Pound Adsorbent*[11]

	Carbon		Resin (Amberlite XAD-4)	
Contaminant	Breakthrough	Saturation	Breakthrough	Saturation
TNT	0.098	0.125	0.020	0.050
RDX	0.300	0.550	0.236	0.382
RDX &	0.008	0.048	0.003	0.019
TETRYL	0.002	0.024	0.001	0.006
TNT &	0.125	0.181	0.116	0.278
RDX	0.074	0.090	0.020	0.030
TNT &		0.134		0.179
HMX	0.006		0.002	

*These values are relative to flow rate; influent concentration; ratio of competitive contaminants.[29,30,31]

SOURCE: Heck, R.P. Munitions Plant Uses Adsorption in Wastewater Treatment. Industrial Wastes, 35-39, March/April 1978.

TABLE 17

ANNUAL COSTS FOR CARBON AND RESIN-CARBON SYSTEM[10]

Carbon System

Item	$/1000 gallons	$/year
Carbon	5.55	210,000
Carbon Burning	0.66	25,000
Labor	0.99	38,000
Maintenance, Repair Property	0.64	24,000
Estimated Annual Operating Costs	7.84	297,000
Annual Equipment Allocation	1.06	40,000
Total Estimated Annual Operating Costs	$8.90	$337,000

Notes: 80 gpm
4 Days/Cycle
100 CF Carbon/Column
Equipment Costs-Total-$600,000
Maintenance, Etc. 4%/Annum of Total Equipment Costs
Labor 537 man-hours/Cycle
Equipment Amortization - 15 years

RESIN-CARBON SYSTEM

Item	$/1000 gallons	$/year
Resin	0.42	16,000
Acetone	0.13	5,000
Steam	0.05	2,000
Cooling Water	0.01	400
Carbon	0.77	29,200
Carbon Burning	0.08	3,200
Labor-Resin	0.92	35,000
-Carbon	0.16	6,000
Maintenance	0.95	36,000
Estimated Annual Operations Costs	3.49	132,800
Annual Equipment Allocation	1.59	60,000
Total Estimated Annual Operations Costs	5.08	192,800

Notes: 6.5 Days/Cycle Resin; 15.0 Days/Cycle Carbon
Equipment Costs $900,000
Labor 645 man-hours/Cycle Resin
258 man-hours/Cycle Carbon
Equipment Amortization-15 years

SOURCE: U.S.A. Patent No. 2,487,627. Process for the Decomposition of Styphnic Acid, November 8, 1949.

Heck[11] points out that when activated carbon is used in the treatment of munitions wastewaters, the largest single cost is the carbon itself. Of the $8.90 per thousand gallon of treated water, $5.55 per thousand gallon is carbon cost. In comparison, the resin-carbon system total estimated operating costs are $5.08 per thousand gallon. The resin, which costs $4.50 per pound, is more economical than activated carbon, which costs about $.50 per pound. He concludes that use of the synthetic resin appears to be advantageous when daily wastewater quantities are greater than 54,000 gallons per day.

Stevens et al.[32] found Amberlite XAD-4 effective for the removal of TNT and RDX from munitions waste water. They showed results similar to those we have already cited. In their case, the capacities of XAD-4 were approximately twice the capacity of activated carbon (Filtersorb 300).

Anspach et al.[33] conducted a study that evaluated solid sorbents for sampling and analysis of explosive from water. The sorbents selected for testing are shown below. Based on such factors as commercial availability, mesh size, surface area, and other studies on capacity, the list of materials to be evaluated for their adsorption/desorption efficiency for explosives in water was narrowed down to the following:

- Amberlite XAD-2;
- Amberlite XAD-4;
- Amberlite XAD-7;
- Amberlite XAD-8;
- Ambersorb XE-340;
- Ambersorb XE-347;
- Ambersorb XE-348;
- Porapak R;
- Porapak S;
- Chromosorb 104;
- Surface-bonded C_{18} on silica;
- Filtersorb 300; and
- Baker Cyano Adsorption Columns.

The thirteen sorbents were evaluated for their adsorption/desorption of eight explosives (TNT, 2,4-DNT, 2,6-DNT, RDX, tetryl, PETN, nitroglycerine and picric acid). The optimum sorbent for each explosive then was selected. The studies for TNT, 2,4-DNT and 2,6-DNT indicated that the best three materials were Porapak S, XAD-4 and chromosorb 104. Porapak S was slightly superior to the other resins when overall results for the three explosives were taken into consideration. XAD-4 gave the best results for TNT but was less effective with the DNT's. Chromosorb 104, yielded recoveries comparable to Porapak S and XAD-4, however, a significant portion of the resin dissolved in the acetone. Based on these data, Porapak S was selected as the only sorbent to be included in further optimization studies.

For RDX and Tetryl, XAD-4, XE-347, XE-348, Porapak S and Porapak R gave acceptable adsorption. XAD-4 and Porapak S were the finalists here. Porapak S showed better recovery of RDX than XAD-4. In the case of Tetryl, the order of effectiveness was reversed as can be seen below:

PRODUCT RECOVERY

Resin	RDX	Tetryl
XAD-4	70-93%	75-87%
Porapak S	96-100%	49-57%

In the cases of nitroglycerine and PETN, the best results were obtained with Porapak R and XE-340. XAD-4 and XAD-7 also showed favorable results. Only XE-348 and Porapak R showed acceptable adsorption of picric acid.

Desorption problems were encountered. The conventional anion exchange strong and weak base resins might have proved to be more effective here because of the polar nature of the picric acid.

Summing up the results of their studies, Anspach et al[33] found that for TNT, 2,6-DNT, RDX and tetryl, the recoveries from the sorbents were essentially quantitative. Recoveries of 2,4-DNT, nitroglycerine, PETN, and picric acid were 85, 68, 52, and 57%, respectively. Once adsorbed by the resins, the explosives remained stable for at least three weeks except for 2,6-DNT and tetryl. Thus, the Porapak resins (R or S) outperformed the styrene divinylbenzene resins (XAD-4 or XAD-2) normally used for sampling of organics from water for treatment of all explosives except tetryl. The data obtained in this study showed that the resins can be reused without loss of adsorption efficiency.

The one potential problem with solid sorbent sampling for explosives is the presence of other organics in the water. These organics could lower adsorption efficiencies, promote reactions or interfere with the analytical methods. Douse[34], in a study similar to that of Anspach, has found Amberlite XAD-7 to be useful for removal of trace explosive compound from handswab extracts.

Van Rossum[35] found that 82 to 83% recovery of o-nitrotoluene by XAD-2 and XAD-4 from tap water could be achieved. Grieser and Pkietrzyk[36] found that nitrophenol and picric acid were retained by XAD-2 to a lesser extent than less polar organics. This was especially true when the pH of the elution solution was increased, primarily because true ion exchange then may begin to take place.

Szachta[37] studied the removal of TNT and RDX, as well as HMX and tetryl, from waste water. Amberlite XAD-4 removed TNT, HMX, RDX, and tetryl from munition waste streams to less than 1 mg/L total nitrobodies. Amberlite XAD-4 had a greater affinity for TNT than for the other nitrobodies. He postulated that at high concentrations of nitrobodies, competition for sorption sites on XAD-4 occured and their breakthrough was earlier. TNT was adsorbed more rapidly than the other nitrobodies.

Tenax GC, which has a fairly low capacity as a sorbent,[38] has been shown to remove 100% nitroglycerin and ethyleneglycol dinitrate from water. Several authors have expressed a concern, however, that in situ reactions occur in the presence of NO_x, ozone, chlorine, bromine, etc., so that the organics recovered from the Tenax GC are not necessarily those that originally were adsorbed.[33,39,40]

USE OF RESIN TECHNOLOGY TO TREAT HAZARDOUS METAL FINISHING WASTES

This section examines application of ion exchange technology to treatment of four major classes of metals finishing wastes:

- Chromium Plating and Anodizing Wastes
- Nickel Recovery
- Precious Metals
  - -Gold
  - -Silver
  - -Platinum Group Metals
- Miscellaneous Applications
  - -Cyanide Baths
  - -Other Metals.

Chromium Plating and Anodizing Wastes

This subject is addressed by a specific system because of the very extensive use of ion exchange for purification of these wastes.[3,4] A detailed list of references on the use of ion exchange for the treatment of spent chromic acid plating and anodizing baths has been presented by Gold,[4] and are shown in Section 6 of this report.[41-63]

A major problem in the use of ion exchange for treating spent chrome baths is the attack on the resins by strong oxidizing agents such as chromic acid.[4,43,64] For this reason, macroreticular and highly cross-linked resins are often preferred; however, for those resins the waste stream must be diluted to concentrations below 200 mg/l of chromic acid.

The reaction that occurs when spent plating and anodizing baths are passed through a bed of strong cation resins in the hydrogen form is as follows:

$$nR^{-}H^{+} + M^{n+} \longrightarrow R_n^{-}M^{n+} + nH^{+}$$

where R^{-} is the resin and M^{n+} is the contaminant metal. The cation resins are regenerated with sulfuric acid. Approximately 20 pounds of 66° Baume sulfuric acid per cubic foot of resin applied as a 10% solution through the bed are commonly used. The resin is then rinsed with water until excess sulfuric acid is removed and replaced into the service cycle.[4]

Stromquist and Reents[43] showed, for spent chromic acid plating bath solutions containing trivalent chromium and iron, approximately 60% of trivalent chrome was removed by ion exchange allowing the bath to be reused. For an aluminum anodizing solution containing Al_2O_3 and small amounts of trivalent chromium, aluminum concentrations in the effluent was less than the Al_2O_3 of the original solution. Morrison[59] found that for anodizing baths, the cation-exchange treatment resulted in a 94.8% removal of trivalent chromium, 99.5% removal of iron, and 99.8% removal of aluminum.

Rinse waters vary in composition, depending upon the rinsing technique employed. Chromium plating and anodizing rinse water may contain 20 to 100 ppm of chromates and have pH in the range of 2 to 3. Basic treatment involves deionization using an anion exchange resin in the hydroxide form followed by a cation exchange resin in the hydrogen form. Sulfuric acid is used to regenerate the cation exchange resin and sodium hydroxide is used to regenerate the anion exchange resin. Waste caustic which contains the recovered chromate is passed over a sulfonic acid cation exchange resin such as the macroreticular Amberlite 200 in the hydrogen form to convert the recovered chromate to chromic acid, which is then returned to the anodizing bath or to the plating bath after concentration in an evaporator.

This approach of passing the water through the anion exchanger first minimizes possible oxidative attack on the anion resin. On occasion, a carboxylic acid cation exchange resin, such as Amberlite IRC-84 or IRC-50 may be used instead of the sulfonic resin because of the higher capacity.[3]

In a typical application, running an Amberlite IRA-400-200 Two-Bed system to exhaustion (1 to 2 ppm) resulted in a recovery of about 4 to 6 pounds per cubic foot of the Amberlite IRA-400.[3] Nashashima[65] also has studied anion exchange removal of contaminants. McGarvey[66] has described the use of a macroreticular resin to treat the following chromic acid waste:

- Chromic Acid--220 grams/liter;
- Copper--19 grams/liter;
- Iron-- 12 grams/liter; and
- Trivalent Chromium--12 grams/liter.

After 175 exhaustion cycles during which the resin treated 25,000 gallons of chromic acid solution, the resin showed an increase in moisture content of only 20%, i.e., from 50% to 61% but there was no serious reduction in physical stability. Under the same condition conventional gel type resins dehydrate after only 25-50 cycles.

In another study, McGarvey and Fisher[67] examined prolonging the life of the dilute chromate bath used in zinc bonderizing processes by removal of polyvalent cation contaminants with a cation exchange resin. Coston[68] and Stromquist and Reents[43] had shown the utility of this process as early as 1950 for concentrated chromic acid baths. The purpose of the McGarvey-Fisher work was to replace divalent ions in the bath by hydrogen, thus regenerating the acid and preventing phosphate precipitation. The macroreticular cation exchange resin, Amberlite 200, was used because of its resistance to degradation by hot chromic acid. The effectiveness of this approach in terms of acidity, solids removal, as well as Zn^{++} and Cr^{+++} removal is shown in Table 18.

Ayuzawa et al.[69] also have conducted studies on the degradation of ion-exchange resins by chrome plating waste solutions. The ion-exchange approach to treatment of chromium plating wastewater also has been examined by Hozaki et al.[70]

Kunin[3] also has reported out that 50 gallons per cubic foot of spent chromic acid can be treated using a flow rate of 1 gpm, employing 10% H_2SO_4 as the regenerant at a level of 20 pounds per cubic foot. giving a product suitable for reuse. He states that the use of countercurrent regeneration reduces

the regeneration level and increases purity. Many plating operations employ this system for chromium recovery and find it far more economical than disposing of the waste and purchasing new chromic acid.

The countercurrent regeneration process is marketed by Eco-Tec Limited, a Canadian firm, using a system developed by Hunter et al.[71-74] The process called "reciprocating flow ion exchange" uses very short resin columns (about 3 inches) and rapidly recycles the contaminated regenerant and rinse solutions through automatic reciprocating valves (less than 30 minutes). These are assembled into units of a few feet in depth that operate on cycles of several hours automatically, requiring little or no supervision. In this manner, the resin bed height is kept to about the same size as the reaction zone in a conventional ion exchange bed. The short bed obviously requires rapid recycling, but also allows the use of fine mesh resin, thereby increasing the ion-exchange efficiency, and allowing treatment and production of higher concentrations.[4,61] Eco-Tec has installed over 100 units of this type for the treatment of chromic acid plating rinse waters and spent baths.[4]

In one commercial application, the consumption of chromic acid was reduced approximately a factor of ten and the concentration of chromic acid in the waste effluent reduced to less than 1 ppm.[74] Eco-Tec also regenerates units returned by small platers. A group at Princeton University is working on a rental concept for hazardous waste control for small platers. The project involves delivering ion exchange units, usually mixed beds, to platers who deionize their rinse waters. The metals in the rinse waters are concentrated on the resins usually to a 100-fold concentration. Once the resins are exhausted, the units are returned to a central place for regeneration. Metals are recovered by suitable processes usually electrolytically.[64] In a similar manner, Eco-Tec serves about 200 Canadian plants.[77]

Another unique system being developed by Life Support Systems, Inc., Stamford, Conn., for the reclamation of chromic acid[75] consists of a truly continuous system in which the treatment and regeneration processes occur simultaneously in different parts of the unit. The system uses an endless belt containing the ion-exchange resin. The belt moves over rollers from one part of a wastewater treatment and rinse tank to the regeneration tank.[4]

Aluminum anodizing solutions were discussed briefly above. Chromic acid baths used in aluminum anodizing pose waste problems similar to those in plating. Fortunately, the chromic acid concentration of an anodizing bath is approximately one-third that of a plating bath. This condition permits use of cation exchanger for rejuvenating the bath without prior dilution.[3] Typical chromic and anodizing baths to be rejuvenated by a cation exchange resin contain approximately 100 grams CrO_4^{-2} and 10 grams Al_2O_3 per liter of solution, as well as a small amount of trivalent chromium. A resin such as Amberlite 200, used according to conditions described for the chromic acid plating bath, can treat more than 30 gallons of the anodizing bath per cubic foot of ion exchanger. Aluminum is removed more efficiently and the treated bath will contain considerably less than one gram per liter of impurities.[3]

TABLE 18

CHARACTERISTICS OF CHROMATE BATH BEFORE AND AFTER ION EXCHANGE TREATMENT

Characteristic	Fresh Bath	Used Bath	
		Before Treatment	After Treatment
pH	2.55	4.10	2.55
Total solids, ppm	232	376	237
Chromium, ppm as CrO_3			
VI (CrO_4^{-2})	98.1	62.9	62.9
III(Cr^{+3})	0.40	0.90	0.00
Total hardness, ppm as $CaCO_3$	22	51	>1.0
Zinc, ppm as Zn	>1.0	25	>1.0
Acidity, normality			
Free acid (pH 4.2)	0.00213	0.00	0.00242
Total acid (pH 8.8)	0.0049	0.0024	0.0049
Phosphorus, ppm as PO_4	122	156	156

A 1978 patent by Etzel[79] talks about the possible removal of chromium and other multivalent heavy metals from metal plating wastes by the use of an exfoliated vermiculite. This material, which has a cation exchange capacity of about 0.8 Meq./gram, less than 20% of a synthetic cation exchanger, is a vermiculite ore that has been expanded either chemically or thermally to separate the aluminosilicate platelets of the vermiculite structure. The magnesium ions between the mica layers are the exchangeable ions.

The removal of iron impurities from spent chromium-plating solutions is important. Rodionov et al.[80] have shown that this can be accomplished effectively through the use of ion exchange resins. Their colleagues[81] have shown that a phenol-formaldehyde resin also could be used to extract chromium ions from the wastewater of electroplating plants.

The technology of using ion exchangers and adsorbents as precoat filters is still in the process of development for various uses. Kunin[82] has shown that EcoSorb A, when an influent of 0.050 ppm Cr^{++} in tapwater is put through it, will remove the Cr^{++} to less than 0.02 ppm in the effluent after 1400 bed volumes have been passed through it. In the case of CrO_4^{-2}, the results of a 25 ppm influent through Ecosorb R were 0.09 ppm effluent after 800 bed volumes and the concentration rose sharply thereafter.

Nickel Recovery

Gold[4] has stated that nickel can only be recovered from nickel-plating rinse waters by ion exchange if the rinse waters are segregated.[47,59] A typical nickel recovery system uses a cation exchanger operation in the hydrogen cycle to remove the nickel ions.[59] Since most nickel baths use nickel sulfate, effluent from the cation exchanger is eluted with sulfuric acid and the regenerant effluent containing concentrated $NiSO_4$ is returned to the plating tanks. The operating capacity for the strong acid cation resins range form 1.2 to 1.8 pound of Ni recovered per cubic foot of resin. The resin is regenerated with 6 to 10 pound H_2SO_4 per cubic foot of resin in a 10 percent solution.

Kunin[3] has discussed the recovery of metal complexes by Amberlite IRA-400 and states that the nickel cyanide complex, $Ni(CN)_4^{-1}$ shows a recovery capacity of 0.1 grams of metal per gram of resin. Waltz[16] has shown Amberlite IRC-718, a macroreticular chelating resin, to have a capacity of 0.7 lb/ft^3 of nickel at a pH of 4.

Leischkov and Mitev[82] have reported on the adsorption of nickel ions on a thermally activated natural sorbent. Hsu et al.[83] described the recovery of nickel from electroplating wastes using an ion-exchange resin. Dillman[14] suggests that nickel can be removed by a weak acid resin at pH values of 5 to 9 and a weak base resin (when complexed) at pH values of 4 to 7.

Calmon[84] suggests that specific ion exchange resins could be prepared for nickel removal using the following chemical groupings:

- dimethyl glyoxine;
- thiol;
- 8-hydroxyquinoline; and
- Beta-diketone;

Kunin[82] reported that the precoat filter, ECOSORB A, leaked 0.15 ppm after the passage of 1400 bed volumes of 0.20 ppm nickel solution. The Etzel exfoliated vermiculite cation-exchange resin will remove nickel from plating wastes.[79] In an example, a solution containing 3 mg/l. each of copper, zinc, and nickel was passed through a vermiculite bed upflow at a rate of 2 ml/min. The bed was 12 inches high and used a volume of 28 ml, with a surface of 0.11 inches. Table 19 shows the metal concentration in the effluent as a function of the number of cumulative liters of effluent.

Precious Metals

Precious metals are generally present in solution as anionic complexes most frequently as cyanides. Since these complexes are highly charged, anion exchange resins will concentrate them readily and are therefore the preferred method of precious metal recovery.

Gold

Gold cyanide complexes are the most common waste in the gold plating industry. Studies involving the recovery of gold from cyanide solutions were first done by S.J. Hussey in 1949[85] using Amberlite IR-4B, a phenolic weakly basic anion exchange resin. In 1953, F.H. Burstall, P.J. Forrest, N.F. Kember and R.A. Wells[86] reported the adsorption of gold from a cyanide solution using Amberlite IRA-400, a strongly basic anion exchange resin. They attained capacities of up to 0.0297 grams of gold per gram of resin. They observed that the presence of sulfate had no effect on the adsorption of gold, but the capacity of the resin for gold was decreased by the presence of thiosulfate or thiocyanate ions. Table 19 indicates the metal concentrations vs volume of effluent and Table 20 illustrates the capacity of an anion exchange resin.

They were able to elute 99.9% of the gold from the resin using acetone containing 5% HCL and 5% water. This elution system had two drawbacks: (1) yielded a dilute eluate and (2) the use of acetone presented flammability problems. Other gold elution systems have been studied, but their effectiveness has generally been poor, and incineration of the resin is the most widely used method for recovering gold from ion exchange resins.[87]

The high value of the recovered material and the high capacity of the ion exchange resin for gold justifies one-time use of the resin easily. High quaternary amine capacity at the lowest cost per quaternary amine unit and good operational characteristics are the important properties to consider when selecting an ion exchange resin for gold recovery. For this reason, Amberlite IRA-400 in either the chloride or the hydroxide form has been widely used by the plating industry for this application. If the stream being treated can contain gold in both the cationic and the anionic forms, then the use of Amberlite MB-1 resin, a mixed bed of Amberlite IR-120 cation exchange resin and Amberlite IRA-400 is suggested by Rohm and Haas.[87] Before designing a unit to recover gold, a laboratory study to evaluate the particular stream in question should be conducted. This study will determine whether a single anion exchange resin will be effective and whether there are interfering anions in the stream that adversely affect the capacity of the resin for gold. Recovery of gold by incinerating a resin, requires a temperature of 500 to 600° C in an oxygen enriched atmosphere. Without sufficient oxygen available,

TABLE 19

METAL CONCENTRATIONS VS VOLUME OF EFFLUENT

Volume of Effluent (cumulative)	Metal Concentration in effluent (mg/l)		
Liters (l)	Cu	Zn	Ni
5	0.00	0.00	0.00
10	0.03	0.03	0.03
12	0.05	0.05	0.05
15	0.075	0.0125	0.075
18	0.04	0.175	0.04
21	0.125	0.725	0.075
24	0.15	2.10	0.10
27	0.4	0.80	0.4
31	1.2	1.5	0.7
35	2.2	2.3	0.95
38	1.95	2.4	1.1

TABLE 20

METAL/COMPLEX CAPACITY OF

AMBERLITE IRA-400

Metal	Complex	Capacity grams of Metal/g. Amberlite IRA-400
Gold	$Au(CN)_2^{-1}$	0.7
Silver	$Ag(CN)_2^{-1}$	0.3
Copper	$Cu(CN)_4^{-3}$	0.08
Iron	$Fe(CN)_6^{-1}$	0.05
Cobalt	$Co(CN)_6^{-3}$	0.08
Nickel	$Ni(CN)_4^{-2}$	0.1
Zinc	$Zn(CN)_3^{-3}$	0.08

the resin chars but is not reduced to ash. There are reports that some of the gold can volatilize while the resin is being washed. Precautions should be taken, therefore, against losing gold "up the stack."[87]

Laboratory studies have shown that Amborane reductive resins, Amborane 345 and Amborane 355, will remove gold chloride complex from solution. It is then recovered by roasting the resin at 500 to 800°C.[87] Law et al.[88] have reviewed the various techniques for recovering gold after its cyanide complex is adsorbed on anion exchange resins.

Calmon[84] has discussed the use of a quaternary polyvinylpyridine anion exchanger for the recovery of gold from cyanide solutions. He also described a polyisothiouronium resin, SRAFION NMRR, for this purpose.[89] In acid solutions, removal of gold was over 99%. The resin was ineffective at alkaline pH values. The total capacities of this exchanger for various precious metals were reported as follows (grams of metal/dry gram of resin:

- gold--0.85;
- platinum--0.50;
- palladium--0.30;
- iridium--0.30; and
- rhodium--0.20.

Owens claims that the recovery of gold from plating rinse waters with ion exchange resins is almost standard practice in the plating industry. Strongly basic anion exchange resins such as Amberlite IRA-400 and Amberlite IRA-900 are most commonly used; however, all of the other strongly basic Amberlite ion exchange resins have been used at one time or another for this purpose, the choice depends upon operating conditions.[90]

McGarvey and Ungar[19] have described a macroporous chelating resin, Ionac SR-3, which is highly selective for precious metals such as gold and others in the platinum group from acid solutions. Base metals such as iron, copper, lead, etc. do not react at all with this resin and do not interfere with the selective process. The noble metals are very strongly attached to the resin, yet their recovery presents no difficulty. For example, one microgram of gold dissolved in one liter of slightly acidified water was completely recovered with the aid of Ionac SR-3. Furthermore, even after adding hundreds of milligrams of nickel and copper to the solution, precious metal recovery was complete to the exclusion of the other metals as shown below (grams per liter capacity of Ionac Sr-3):

- Gold--150;
- Platinum--65;
- Palladium--58;
- Iridium--25; and
- Mercury--150.

The resin is currently used on a commercial scale in recovering gold from waste effluents and rinse waters of acid goldplating solutions. It is also suggested for noble metal extraction from ores and wastes, the separation of noble from base metals, the recovery of spent catalysts, the concentration of very dilute solutions containing noble metals, and the refining of noble metals.

Silver

In plating waste, silver is generally present as the anion silver cyanide complex $Ag(CN)_2^-$. Both strongly basic and weakly basic resins have been found useful in the recovery of the silver, while 5 molar NaCl has been used successfully to elute the silver from the resin. The ammonium, sodium or potassium salts of cyanide, thiocyanate, and thiosulfate ions seem to be the most promising for elution.[87]

Burstall, et al. used Amberlite IRA-400 and observed a maximum capacity of 0.15 gm/gm resin when adsorbing silver cyanide. Using 2N potassium thiocyanate as the elution stream, they recovered 100% of the silver from the resin.[86] Silver was then recovered from the eluent by electrolysis. Silver has also been recovered from Amberlite IRA-400 resin by incineration.[87]

A weakly basic resin suggested for the recovery of silver is Amberlite IRA-68, a gel type acrylic resin. The resin is first placed in the bisulfate by exposure to 4% sulfuric acid. The silver-containing waste stream is passed through the bed and a solution of potassium thiosulfate is introduced to elute the silver.[87]

Dr. Howard W. Chou of the Eastman Kodak Company,[91] used Amberlite IRA-68 and Amberlite IRA-400 to remove silver from wash water. Countercurrent (upflow) regeneration was utilized. Dr. Chou included a variety of macroreticular and gel type resins-Type I strongly basic, Type II strongly basic, and weakly basic in his study and found that only Amberlite IRA-400 and Amberlite IRA-68 resins had acceptable capacity after three regeneration cycles. A silver breakthrough study of both resins was conducted using a solution containing approximately 15 mg/l of silver. This comparison showed that Amberlite IRA-68 had a lower silver capacity than Amberlite IRA-400. Regeneration of the resins with 30% ammonium thiosulfate required six bed volumes to remove 90% of the silver from the Amberlite IRA-68, while the same volume of regenerant removed only 60% of the silver from the Amberlite IRA-400. In succeeding cycles, the capacity of Amberlite IRA-400 for silver dropped from 50 grams per liter to 20 grams per liter when the resin was regenerated with 30% ammonium thiosulfate. A second regenerant of 5% sulfuric acid added on the third cycle restored the resin capacity to 45 grams per liter. The average capacity of Amberlite IRA-68 over 8 cycles was 27 grams per liter when regenerated with 30% ammonium thiosulfate alone.[91]

The silver contained in the ammonium thiosulfate can be recovered by trickling it through a chemical cartridge prior to discharge. If the silver is recovered electrically, the ammonium thiosulfate solution can be reused with no apparent loss in activity.[87]

Balakin et al.[92] have made anion exchange resins that are based on pyridine and quinoline. These resins have been shown to be effective in the removal of gold and silver from cyanide solution. Vyalkov et al.[93] have examined a variety of anion exchangers for their ability to extract silver from cyanide

solutions. In a rather interesting variation of this theme, Urasova et al.[94] have studied the effect of flotation agents on gold sorption from cyanide media, using the Russian anion exchanger AM-2B and flotation of the exchange resin.

Platinum Group Metals

Strongly basic anion exchange resins have proven useful in recovering platinum group metals from plating waste streams containing these metals as chlorides. One stream studied was a combined primary and final rinse containing 5.65 ppm of palladium and 1.54 ppm of copper at a pH of 2.04. Palladium was present as the anion complex (probably a complex palladium chloride) and could be separated from the copper cation by passing the stream through a strongly basic anion exchange resin. Excellent removal was shown through analysis of the column effluent which contained only 0.1 ppm of palladium. Regeneration was accomplished with 4% sodium hydroxide.[87]

Platinum and palladium, as the chloride complexes, may be removed from solution by Amborane-345 and recovered by incinerating the resin. This area is still in an early stage of development.[87]

Miscellaneous Applications

Cyanide Baths

Cyanide baths and the removal of precious metal from them were discussed in the preceeding section. In this discussion, the use of resins to remove other contaminants in cyanide baths will be discussed.

Presented in Table 20 was the capacity of the strong base anion exchanger, Amberlite IRA-400 for several metallic complex cyanides. In many plating industries, the operating area may include several different plating baths, the wastes of which cannot be easily segregated. Chromium, copper and nickel plating are commonly performed in the same location, with zinc and copper cyanides frequently present. An average composition of mixed plating rinse waters is as follows:[3]

- Copper--13 ppm;
- Zinc--9 ppm;
- Nickel--8 ppm;
- Chromium--3 ppm;
- Cyanide --8 ppm;
- Phosphate--25 ppm;
- Total Dissolved Solids--540 ppm; and
- pH--2.7 ppm.

Kunin cites various ion exchange combinations and procedures for these wastes and claims that a Monobed of Amberlite IRA-410 and IR-120 has been employed to treat such waste waters quite successfully. In this case, the anion exchange resin must be regenerated in two stages, using sulfuric acid to break the complex followed by sodium hydroxide solution.

Rohm and Haas[95] describe a process for selective cyanide removal in which cyanide is converted to ferrocyanide or ferricyanide and removed by passing the solution through a column of ion exchange resin. Removal of these cyanide complexes selectively by ion exchange allows other anions to pass through the resin bed. This system utilizes the capacity of the resin for cyanide removal only, increasing the amount of water that can be treated with a given amount of resin. Amberlite IRA-958 is an acrylic, strongly basic anion exchange resin designed to remove these cyanide complexes. Because this resin is acrylic and macroreticular, it will not foul as readily as gel-type resins.

A unique feature of Amberlite IRA-958 is its ability to adsorb cyanide without adsorbing thiocyanates frequently present in cyanide-bearing wastes. Cyanide can be converted to Prussian blue by acidification and precipitation of the regenerant with an excess of iron salts. The Prussian blue thus becomes a salable by-product of this process.

More exotic cyanide ion exchangers have been described by Kokufuta[96,97] and Balakim[98,99]. The former has prepared and studied copoly (styrene-divinylbenzene) covalently bonded protothemin-mono-N-histicyclamide as a cyanide anion exchanger. The latter has examined picolinium, quinolinium and benzoylnidinium anion exchangers for complex cyanides. Bolotova[100] has studied the relationship of the mass transfer rate with ion-exchange resin grain size and temperature in a cyanide solution-anion exchanger system.

Other Metals

Removal of aluminum in anodizing baths can be achieved with Amberlite IR-120 PLUS or Amberlite 252. Capacities, depending upon the type and concentration of acid in the bath (sulfophthalic, sulfosalicylic, oxalic or sulfuric acids), and the aluminum concentration, generally vary from 3.2 to 12.8 grams per liter of resin. Oxalic acid baths are the exception, achieving capacities of more than 19.2 grams per liter. Regeneration is accomplished with 15 to 20% sulfuric acid at 320 to 400 grams per liter; however, only the first half of the regenerant is used for neutralization and precipitation. The last half is recycled to be the first half of the following regeneration.[77]

McGarvey and Fisher[67] have used an ion exchange process to concentrate dilute wastes produced in the rinse operation in the zinc bonderizing process. This treatment permits recycle of the water and eliminates the discharge of zinc and phosphate. Use of a strong acid cation exchange resin in the hydrogen form followed by a weak base anion exchange material yields a 75-fold reduction in waste volume and a good quality water produced for reuse in the rinse.

Goddard[101] has described the application of the Intensive Fractionation Process (IFP) that was developed by Vajna[102] to recover copper from copper plating rinse waters. In the IFP, a very strong (2 to 8 N) solution is contacted a number of times with a loaded ion exchanger until the equilibrium is driven to the required level. The approach is similar to that of a counter current ion exchange process except that the solution phase moves, rather than the resin phase, thus simplifying the plant operation. Some rinse waters from copper-plating operations have copper concentrations in the range of 200 to 500 mg/l. Cation exchange can be used to reduce the copper level to less the 1 mg/l, which is generally acceptable for discharge. Use of the IFP system

for regeneration of the copper-loaded resin makes it possible to produce a copper solution containing 100 to 120 g/l Cu which, in many cases, is reusable. The free acid concentration in the recovered product is low at 0.1 to 0.2 N.

USE OF MEMBRANE TECHNOLOGY TO TREAT TOXIC AND HAZARDOUS METALS FINISHING WASTES

This section examines three different general classes of membranes:

- Size exclusion membranes
  - -Reverse osmosis
  - -Ultrafiltration
  - -Dynamic membranes
- Ion exchange membranes
  - -Donnan dialysis
  - -Electrodialysis
- Liquid membranes
  - -Coupled transport
  - -Unsupported liquid emulsions.

Each method will be discussed in general terms, including history, limitations, and current industrial applications, both in the industries of study and in related industries. The last evaluations of specific products currently available and those in development follow. These are evaluated by type of membrane, innovation, demonstration status, and economic considerations. The application of membranes in the plating and munitions industry are viewed in Tables 21 and 22.

Size Exclusion

Reverse Osmosis-Description and History--Reverse osmosis is a process in which an applied pressure is used to change the direction of the normal osmotic flow of water across a semipermeable membrane.[103] In normal osmosis, pure or dilute solvent flows across the membrane to the more concentrated side. Flow from the concentrated side back to the dilute side is prevented by the osmotic pressure of the concentrated solution. Osmotic pressure is a coligative property of the solution, that is, it is directly proportional to the concentration of the dissolved materials. For water to flow in the reverse direction, pressure greater than the osmotic pressure must be exerted on the solution. In reverse osmosis, solvent crosses from the concentrated solution to the dilute, producing a very concentrated solution and a purified solvent.

Reverse osmosis is not a filtration technique like ultrafiltration or microfiltration, but a true membrane process. Pore sizes range from 1 to 10 angstroms and will exclude any molecule with a molecular weight larger than about 300 angstroms.

TABLE 21

CURRENT REVERSE OSMOSIS INSTALLATIONS IN THE ELECTROPLATING INDUSTRY*

TYPE OF BATH	TYPE OF MEMBRANE	CONFIGURATION	NUMBER OF INSTALLATIONS	ZERO DISCHARGE
Bright nickel Nickel sulfamate Watts nickel	Cellulose acetate	Spiral-wound	150	yes
Copper sulfate	Polyamide Cellulose triacetate Thin-film composite	Hollow-fiber Spiral-wound	12	no
Zinc sulfate	Thin-film composite	Spiral-wound	1	90% recovery
Brass cyanide	Polyamide Cellulose triacetate	Hollow-fiber	5	90% recovery
Copper cyanide	Polyamide	Hollow-fiber	2	90% recovery
Hexavalent chromium	Thin-film composite	Spiral-wound	Under investigation	

*Source: (106) as of April 1984, according to Peter S. Cartwright

TABLE 22

EVALUATION OF CURRENTLY AVAILABLE MEMBRANES

HIGH DEMONSTRATION STATUS

COMPANY	TYPE OF MEMBRANE	CONFIGURATION AND COMPOSITION	ACTUAL INSTALLATIONS	SUPPORT TECHNOLOGY	ECONOMIC CONSIDERATIONS
Osmonics	Reverse osmosis	Spiral wound Cellulose acetate	Over 200	Evaporation & ultrafiltration	Payback 6-12 months
Memtek U.S.A.	Ultra-filtration system	Tubular Polysulfone	50	Precipitation	Highly variable
Lancy	Electro-dialysis	Stack Divinylbenzene-polystyrene	43	---	Payback 1.3 years for nickel
Filmtec	Reverse osmosis	Spiral wound Thin-film composite	Some	---	Payback 18 months
Romicon	Reverse osmosis	Hollow fiber Various	Proprietary	---	---

MODERATE DEMONSTRATION STATUS
(On the market currently)

COMPANY	TYPE OF MEMBRANE	CONFIGURATION AND COMPOSITION	ACTUAL INSTALLATIONS	SUPPORT TECHNOLOGY	ECONOMIC CONSIDERATIONS
HPD	Electro-dialysis	Stack Divinylbenzene-polystryene	2-3	---	---
Ionics	Electro-dialysis	Stack Polysulfone Cellulose	1	Uses Reversal	---
Abcor	Ultra-filtration	All types Various	1 (Munitions)	---	0.25-0.5 M per 100,000 gal/day

TABLE 22 (continued)

EVALUATION OF CURRENTLY AVAILABLE MEMBRANES

MODERATE DEMONSTRATION STATUS

COMPANY	TYPE OF MEMBRANE	CONFIGURATION AND COMPOSITION	ACTUAL INSTALLATIONS	SUPPORT TECHNOLOGY	ECONOMIC CONSIDERATIONS
Dow	Reverse osmosis	Hollow fiber Cellulose acetate	Several	---	---
Ionac	Electro-dialysis	Sheets Divinylbenzene-polystryene on polyolefin	Unsure, only manufacture membranes	---	---
DuPont Nafion	Electrol-ysis	Sheets Perfluorosulfonic Acid	A few	---	---
Innova	Electrol-ysis	Sheet Proprietary	Several for hexavalent chrome	---	Payback 2.5 years
RAI	Ion exchange	Various Polypropylene felt grafted with monomers	Several	---	---
RCC	Seeded reverse osmosis	Tubular Cellulose Acetate	Several (Heavy Metals)	Evaporation	---
Neptune Microfloc	Dynamic	Tubular "Thermoplastic"	Lab tested	---	---

MODERATE TO LOW DEMONSTRATION STATUS
(Pre-manufacturing)

COMPANY	TYPE OF MEMBRANE	CONFIGURATION AND COMPOSITION	ACTUAL INSTALLATIONS	SUPPORT TECHNOLOGY	ECONOMIC CONSIDERATIONS
Bend	Reverse osmosis	Hollow fiber	Pre-manufac-turing	None	$10-20/sq. ft.
Bend	Liquid sheets, beads	Hollow fiber, Pre-manufacturing	Field tested for hexavalent	Chemical	$1-2.50 per

TABLE 22 (continued)

EVALUATION OF CURRENTLY AVAILABLE MEMBRANES

MODERATE DEMONSTRATION STATUS

COMPANY	TYPE OF MEMBRANE	CONFIGURATION AND COMPOSITION	ACTUAL INSTALLATIONS	SUPPORT TECHNOLOGY	ECONOMIC CONSIDERATIONS
Albany Int'l	Reverse osmosis	Hollow fiber Polysulfone	Pre-manufacturing	---	---
Memtek Ontario	Mobile reverse osmosis system	Various	Field tested	Various	---
Texas ROMEC	Mobile reverse osmosis system	Mott stainless steel/Toray PEC-1000	Field Tested	Various	---
General Electric	Liquid	Proprietary	Lab tested	---	---

EVALUATION OF CURRENTLY AVAILABLE MEMBRANES

NO DEMONSTRATION STATUS -- POTENTIAL APPLICATION

COMPANY	TYPE OF MEMBRANE	CONFIGURATION AND COMPOSITION	ACTUAL INSTALLATIONS	SUPPORT TECHNOLOGY	ECONOMIC CONSIDERATIONS
SFEC	Dynamic	Tubular Zirconium oxide/ sintered carbon	None	---	---
Carre	Dynamic	Tubular Zirconium oxide/ stainless steel	None	---	---
Mott	Inorganic	Stainless steel	None	---	---

Historically, the first application, and still by far the largest, is desalination of water. In 1960, Loeb and Sourirajan produced the first thin-skinned cellulose acetate membrane in a tubular design which had a sufficient flux rate to make desalination practical.[103] Shortly afterwards, Dupont produced a hollow-fiber configuration using a membrane made of aromatic polyamide. The spiral-wound configuration was developed by Westmoreland (and later Bray) for a more efficient design. Another development around the same time was a new more chemically resistant membrane, called a thin-film composite membrane, made of cellulose esters. Low pressure thin-film composite membranes have also been developed for use with wastes of moderate osmotic pressures.

Essentially, three types of membrane materials are being used: cellulose acetate (CA), aromatic polyamides (PA), and thin film composite (TFC). There are three types of configurations available: tubular, hollow-fiber, and spiral-wound. Reverse osmosis is considered to be a mature technology.[103] Most recent work has been done in modifying the systems that incorporate the membranes or modifying slightly the composition of the polymer in order to find further applications for reverse osmosis.

Inherent Problems--Three problems that must be overcome to apply reverse osmosis to a given separation problem are the same as for membranes in general:

- o low flux
- o fouling and adsorption
- o chemical or biological degradation.

Cellulose acetate is known to degrade with time. It is subject to biological attack and cannot tolerate a pH of higher than 7.5. Belfort also reports leakage of feed constituents as a problem.[104] Polyamide, while operating over a wider pH range in both basic and acidic media, cannot tolerate free chlorine in water. Fouling also has been a problem.[104] New sulfonated polysulfone membranes have very high chlorine resistance.

Fouling can affect all types of membranes under different conditions, particularly in the treatment of wastewater. For example, rejection of chromate ion is good under basic conditions, but if any aluminum hydride is present it will precipitate and foul the membrane.[104]

Current State of the Art--Available data indicate that reverse osmosis has a high demonstration status for treating electroplating wastewater. Reverse osmosis is currently being used to recover brass, hexavalent chromium, copper, nickel, and zinc. Zero discharge is the ultimate goal of these systems with the pure water and the concentrate being recycled in the process.[105] Rinses after Watts nickel, bright nickel, and nickel sulfamate all can be treated successfully in a zero discharge system; however, duplex nickel, a semi-bright nickel, cannot.[105] All three types of membranes have been applied under various conditions. No one membrane can handle all types of electroplating wastes. The two configurations used have been hollow fiber and spiral wound. Table 21 shows a summary of installations. Most wastes require pretreatment, usually a five micron microfilter.[106] Cartwright also sees applications of reverse osmosis to tin/lead fluoroborate rinse waters. He does not believe reverse osmosis can successfully treat zinc cyanide rinse waters on a commercial scale and

claims the osmotic pressure of the zinc cyanide solution is too high to undergo reverse osmosis. Preliminary research has been done by Abcor [107] on zinc cyanide; but, there has been no reported commercial plating operation currently using reverse osmosis for zinc cyanide.

Improvements in the design of reverse osmosis systems have allowed membrane technology to be applied to more complex systems, incorporating pre-treatment to treat chemical spills threatening the groundwater or water found in oil field pits. These systems are designed as mobile units. Detailed descriptions are discussed in the section on evaluation of specific commercially available products.

Advances in polymer sciences, particularly in the thin film composite membrane, will improve the applicability of reverse osmosis. Minor changes in polymers and membrane composition are being examined. Research in reverse osmosis was reported recently at the American Chemical Society National Meeting held in Philadelphia, August 26-30, 1984. (Appendix B) For example, Toray Industries is attempting to improve flux by changing the weave of the fabric support to a tricot weave on their thin film composite membrane. Basic research continues on the reverse osmosis process in an attempt to understand the properties of reverse osmosis membranes. An example of basic research, Dr. Belfort of Rensselaer Polytechnic Institute is researching the fluid mechanics of dilute suspensions in membrane systems.

Reverse osmosis has a high demonstration status in treating electroplating rinse waters and other waste waters. Research continues in three areas:

- Materials Science - Improved polymeric materials
- Engineering -Design of Total Systems
- Basic Research -Understanding the Membrane Process.

Ultrafiltration--Ultrafiltration is part of a continuum of membrane separation techniques that primarily depends on size exclusion. Ultrafiltration membranes are generally not defined by their pore sizes, which ranges from 10 up to 500 angstroms. (See Appendix A.) Rather, ultrafiltration membranes are usually defined by the size of molecule excluded. One reason for this is that these membranes do not have pores of just one size but rather have a spectrum of pore sizes. The size range that divides ultrafiltration from microfiltration has been variously reported to be 100,000 to 500,000 molecular weight units. This report will use Lonsdale's definition that ultrafiltration membranes retain species in the molecular weight range of 300 to 300,000.[103]

The first major advance in ultrafiltration membranes occurred simultaneously with reverse osmosis with the Loeb-Sourirajan cellulose acetate membrane. The final step in the formation of the Loeb-Sourirajan reverse osmosis membrane is to anneal the membrane in water at 80° C and upwards. Unannealed reverse osmosis membranes are good ultrafiltration membranes.

Ultrafiltration membranes are made from a wider selection of polymers than reverse osmosis membranes. Cellulose acetate, polycarbonate, polyvinyl chloride, polyamide, polysulfone, polyvinylidene fluoride, copolymers of acrylonitrile and vinylchloride, polyacetal, polyacrylates, polyelectrolyte complexes, and crosslinked polyvinyl alcohol are used.[103]

There are four basic UF module configurations in current use:

- o Flat-plate thin-channel
- o Tubular thin-channel
- o Hollow-fiber
- o Spiral-wound.

Spiral-wound and tubular modules are similar to the configuration used in reverse osmosis. However, the hollow-fiber configuration is completely different. In ultrafiltration, the membrane skin is formed on the inside diameter of the hollow fiber. Feedwater passes through the bore and product water permeates out through the outer support structure. In reverse osmosis, the membrane skin is on the outer diameter and the product water flows into fiber bore.[108]

All module configurations must maintain high shear rates at the membrane surface to minimize concentration polarization. Pumping is used to maintain the required high shear rates. However, because solutes with molecular weight less than 300 readily permeate the membrane, there is no great osmotic pressure difference between the feed water and the product water. As a result, processing is carried out at relatively low pressures (1-5 atmospheres).

Inherent Problems--Ultrafiltration membranes are made from a wider selection of materials, than membranes for reverse osmosis. Chemical and biological resistance is greater because of this wide selection for various applications. Flux rates are normally high except when there are major fouling problems. Fouling is the principal problem with ultrafiltration membranes. Two things occur when filtering solutions with large macromolecules:

- o certain macromolecules adhere to the walls of the membrane skin
- o a deposition of macromolecules on the surface of the membrane causes resistance to flow by forming a gel layer.

Concentration polarization is a problem with all membrane processes, but especially with ultrafiltration. Sometimes, the macromolecules form a gel. High shear rates appear to mitigate concentration polarization. Modules must also be designed for easy cleaning in order to prevent a decrease in flux from fouling.

State of the Art--Ultrafiltration has a high demonstration status in the electroplating industry and in the overall waste treatment field. In the electroplating industry, ultrafiltration is used in conjunction with other techniques for cleaning up rinse waters. For example, they are used as pre-filters for reverse osmosis units. According to Cartwright [106] five micron filters are generally used as pre-treatment for reverse osmosis units. One system has been designed to remove the chemically precipitated heavy metals by ultrafiltration rather than by flocculation and gravity sedimentation. Research is continuing in areas similar to that of reverse osmosis.

Ultrafiltration has a high demonstration status in many industries: in electropainting, in the food and dairy industry, in separating oils from water, in sterilization, and in the pharmaceutical industry. Ultrafiltration shows a wide versatility when applied to diverse chemical and biological environments that one could extrapolate their use to many applications.

Work is continuing to improve the polymers used. According to Leeper et al.,[109] work is being done on alloy membranes (membranes made of blends of two or more materials). Development has begun on membranes that incorporate specific compounds into the barrier layer to enhance selectivity.

The three areas of research are the same as for reverse osmosis:

- Materials Science
- Engineering Design
- Basic Research.

Dynamic Membranes and Inorganic Membranes

Description and Background--Dynamic membranes use size exclusion and Donnan exclusion to achieve separation as the reverse osmosis/ultrafiltration/microfiltration polymer type and are not a truly separate type of membrane. They differ mainly in the way they are produced. Dynamic membranes encompass the separation range from reverse osmosis through ultrafiltration. Dynamic membranes are generally inorganically based, but there is one organic polymer-based that has been used in treating electroplating wastewaters.

The early research in inorganic dynamic membranes was performed by Johnson at Oak Ridge National Laboratory[110]. His inorganic dynamic membrane consisted of two parts:

- A sintered support made of either carbon, stainless steel, alloys or ceramic material
- One or more dynamic layers made of metal oxides, polymer films or suspended solids.

The sintered inorganic support layer is generally able to stand alone as a microfilter/ultrafilter. The usual configuration consists of tubular modules employing cross flow filtration. The membrane is formed by flowing a feed solution of membrane-forming material tangentially to a clean porous surface at velocities of 5 to 50 feet per second and pressures of 500 to 1200 psi.[109]

Inherent Problems--Dynamic membranes experience problems similar to those of RO and UF, but to a lesser degree in some cases. Inorganic and inorganic based dynamic membranes tolerate high temperatures, some up to 300 degrees Celsius and pH levels of 0-14.[112] Maintenance of flux rate and fouling problems are the same as for equivalent configurations of the thin-skinned polymer types. However, one type of polymer based dynamic membranes is actually formed from adsorbed suspended solids on the pore wall.[113]

State of the Art--Although techniques for the formation of inorganic and dynamic membranes has been known for some time, little work has been done in the application of these membranes to wastewater treatment. In Europe, dynamic inorganic membranes are used widely in the cheese industry because they can be steam sterilized. Inorganic stainless steel filters are used to treat and recycle radioactive wastes [114]. The ZOSS and ZOPA membranes have been used to remove organics from a dye manufacturing process effluent.[110] Only one dynamic membrane has successfully treated electroplating waste streams in laboratory testing.

This technology is not as mature as reverse osmosis/ultrafiltration. New types of membranes are still being developed. At the American Chemical Society Meeting, Dr. Leenaars of University of Technology, Netherlands, reported forming a new membrane of aluminum oxide on a ceramic base which was still in the testing stage [112]. Great potential seems to exist for treatment of hazardous wastes streams because of the chemical resistance and high tolerance of these membranes. Further research should be done in this area, both fundamental research in new types of combinations of materials and in the application of existing commercially available products to hazardous waste treatment.

USE OF ION EXCHANGE MEMBRANES TECHNOLOGY TO TREAT METAL FINISHING WASTES

Electrodialysis

Description and History--Electrodialysis, as its name implies, is a dialytic process, in which an applied electric field is used to draw ions across a membrane.[103] Electrodialysis membranes always come in pairs, one cation and one anion exchange membrane. Early research on this process was performed in the 1930's although commercial applications are generally more recent.

The usual commercial configuration is the stack. The stack consists of pairs of cation/anion exchange membranes with separators and an anode at one end and a cathode at the other. Anions flow toward the anode until they are stopped by a cation-selective membrane and vice versa. As a result there is a series of cells where there is alternate concentration or depletion of ionic species.

Most modern electrodialysis stacks use membranes of essentially the same chemistry. The usual materials used are membranes made of copolymers of divinylbenzene-styrene with an ion exchange group attached to the benzene ring. The cation exchange membrane generally has sulfonate groups attached. The anion exchange membranes generally have quaternary ammonium groups attached as the ion exchangers, much like ion exchange resins.[105]

Inherent Problems--The major limitation of electrodialysis and all other ion exchange techniques is that they can be applied only to separations of ionic species or molecules that can be easily ionized. In particular, organic molecules that cannot be ionized, cannot be treated by ion exchange techniques.

Like the size exclusion membranes, electrodialysis has a major problem with concentration polarization. The anion-exchange membrane can be polarized by organic or inorganic materials. This problem is apparently created by the local pH shift that occurs on the concentrate side of this membrane. This

leads to an increased voltage drop across the stack, which leads to larger power use.[103]

State of the Art--Lonsdale defines electrodialysis as a mature technology.[103] The problem of fouling and concentration polarization mentioned above has been ameliorated by reversing the polarization of the stack. Concentrating compartments become diluting compartments and vice versa. Another system design that is proposed to overcome this problem is the feed and bleed recirculation system.[115] There have been some applications in the electroplating field and many companies that produce electrodialysis systems have one or two installations in the electroplating industry.

One company (installs systems, but does not manufacture membranes) has over forty installations. (See the evaluation on Lancy in the section of the evaluation of specific products.) Therefore, electrodialysis has a high demonstration status in electroplating applications.

Donnan Dialysis

Description and History--Donnan dialysis has been named after F.G. Donnan who described thermodynamic equilibrium conditions of membrane separations back in the 1920's. Donnan dialysis, unlike electrodialysis, uses a single membrane which is either anion or cation permeable.

There is no external driving force like the electric current in electrodiaylsis or pressure in size exclusion separations. The system is driven by the difference in ionic activity on opposite sides of the membrane. For example, in the simplest situation, a metal salt is dissolved on the feed side of a cation-permeable membrane and a concentrated acid is on the strip side of the membrane. Hydrogen ions will diffuse from the high pH solution in the strip side to the feed side. To maintain electric neutrality, the positive metal ions are forced from the feed side to the strip side. Tubular membranes can be used in a shell-and-tube type configuration.[116]

Cation exchange Donnan dialysis membranes are commercially available. In particular, a perfluorosulfonic acid copolymer membrane is currently on the market. Other cation exchange membranes have been made from polystryene-polyethylene and sulfonated polyvinyl chloride.[117] Attempts have been made to produce anion exchange membranes from polyethylene grafted with vinylpyridines or vinylbenzylchloride which are then quaternized with alkyl halides or trialkylamines.[118]

Inherent Problems--The major problem associated with Donnan dialysis is the slow rate of flux through the membrane. Attempts have been made to use countercurrent flow to speed up the process. The rate can be increased by increasing temperature but problems develop with the integrity of the membrane.[117]

Since the driving force of the system for cation exchange Donnan dialysis is a higher hydrogen ion concentration, very low pH is required by the system. The membranes used must be able to survive in a very acidic environment. For example, work done on stripping uranyl nitrate used a three molar solution of nitric acid, an extremely acidic condition.[117]

State of the Art--Donnan dialysis has been applied to industrial treatment. Kelly, Randall, and Wallace report a successful pilot plant trial to treat waste water from the Savannah River Nuclear Power Plant.[117] P.K. Ng reports three successful studies, one by himself and one by John Eisenman on nickel plating solutions and one by Henry Law in gold plating.[116]

Although the principles of Donnan dialysis have been established for a long time, industrial applications of this form of dialysis is in its infancy. Cation exchange membranes are commercially available. Anion exchange membranes are still experimental. The basic problem of low flux has not yet been overcome.

Donnan dialysis is still in the laboratory-pilot plant test stage. It will not gain large scale application until the inherent low flux can be increased.

Other Ion Exchange Membrane Applications--Use of ion exchange membranes in ion exchangers is similar to use of electrodialysis. One system uses a membrane like a ion exchange resin. These membranes are radiation grafted polypropylene felt. They allow water to permeate, but do not allow the ionic species to pass which is the opposite of Donnan dialysis. Instead ions are captured onto the membrane to be stripped later by a rotating cathode. This is a relatively recent configuration. This system is becoming available commercially and has been tested in electroplating operations.[119]

Another system developed in conjunction with an electrode is the Chromium Oxidation and Purification System (COPS). A perfluorosulfonic acid action exchange membrane is used between an anode and a cathode. Metallic impurities such as copper, zinc, and cadmium pass through to the cathode, but trivalent chromium does not. It is oxidized to hexavalent by the anode and is reused in the process tank.[120]

LIQUID MEMBRANES

Immobilized Liquid Transport-Description and History--Liquid membrane systems use a thin liquid film to act as a diffusional barrier between the phase containing the species to be removed and the stripping phase.[121] The species to be removed permeates the membrane, not the solvent. This is the opposite of size exclusion or classical membrane techniques where the solvent permeates the membrane. It is similar in this respect to most ion exchange membranes. The liquid membrane can be either supported or unsupported. Liquid membranes are the newest type of membranes having been first developed in 1968. Most of the research done on liquid membranes has been recent.

When the liquid is immobilized onto a solid support, it is known as an immobilized liquid membrane. Transport through the liquid membrane is usually enhanced by a chemical reagent which reacts or interacts with the species to be removed.

One type of transport is coupled transport. A water-immiscible liquid ion exchange agent is immobilized on a hollow fiber and is held in the pores of the support by capillarity. Ion exchange takes place on one side of this membrane by the organic molecule picking up a metal cation from the feed solution. In order to maintain conservation of charge, a positive hydrogen ion must be released by the membrane into the feed stream for every positive

charge on the metal ion. The metal ion complex is then dissolved in the organic liquid and migrates to the other side of the membrane where there is an abundance of positive hydrogen ions in an aqueous product solution. The organic compound picks up the positive hydrogen ion and releases the metal cation into the product stream. The simultaneous uptake and release of metal cation and positive hydrogen ion is why it is referred to as coupled transport. The driving force is the positive hydrogen ion concentration just as in cationic Donnan dialysis. As long as the pH of the product stream is two pH units lower than the feed stream, regardless of the metal cation concentration, ion transport will occur in the desired direction.[122] Choosing the organic phase allows you to choose the metal cation transported. For example, to remove nickel from a copper solution to purify the bath, one could, in theory, pick the right organic agent and selectively remove nickel while leaving copper behind.

Currently, there are three proposed configurations: hollow fiber, sheets and beads. The hollow fiber configuration appears to be the most advanced and may be the one commercially available first.

Inherent Problems--Although these are very different from other types of membranes, resistance to harsh chemical environments for a long service life and high flux rates are areas where there is still a need for further research.[123]

State of the Art--Immobilized liquid membranes are soon to be commercially available. Development and field testing have been underway for the last eight years. Field testing has been intense in the metals recovery area in electroplating and especially in recovery of copper and chromium.

Unsupported Emulsions-Description and History--Liquid membranes, which have no solid support, are referred to as an emulsion liquid membrane. An example of this is an emulsion of small droplets of water in an oil that contains a chelating agent. This emulsion is placed into the solution that needs to be treated. The metal ionic species that is to be removed will migrate into the little water droplets inside the oil emulsion. The mechanism uses a carrier and is the same as the coupled transport described above. Organic molecules can also be removed by a different type of emulsion liquid membrane. The solute must permeate the film and then react to form a new compound that becomes dissolved in the emulsion. Both of these transport mechanisms are steady-state continuous processes.[123]

State of the Art--Emulsion liquid membranes are an experimental technology at the laboratory stage. Along with other fundamental research, heavy metal recovery is currently being studied.

EVALUATIONS OF SPECIFIC PRODUCTS

In this section, specific products are evaluated based on metal finishing and munitions wastes as well as type of membrane offered, the composition and configurations, the actual installations, support technology, and some general economic considerations. Results are summarized in Table 22.

Reverse Osmosis

High Demonstration Status (Commercially Available)

Osmonics, Inc. produces a spiral wound, cellulose acetate, reverse osmosis membrane. It can tolerate a pH range of 2 to 8. Product literature claims it can be used to treat nickel, chromium, copper, and zinc rinses.[124] It has a high demonstration status especially for nickel rinses. It was reported that they have more than 200 installations in the electroplating industry, including 130 nickel plating operations.[125] Product literature claims that the system would pay for itself in 6 to 12 months. The membrane is sometimes combined with ultrafiltration or evaporation. Osmonics also claims that they have designed a system to treat oily wastes, including soluble and insoluble oils.[126]

Filmtec Corporation produces a thin film composite membrane, using a cross-linked polyamide skin on a polysulfone and is available in a spiral wound configuration. It claims high chemical and biological resistance and can tolerate strong alkali. Filmtec reports actual electroplating installations, but fewer of them than Osmonics, according to David Furukawa. This membrane has been field tested on all types of plating rinse waters. In one paper[127], the company claims that in eighteen months, a Filmtec system would pay for itself in savings when used in nickel plating rinse waters. The Filmtec membrane has many additional applications in other industries. Film Tec has also developed two types (FT40, FT50) of low pressure charged membranes.

Romicon produces hollow fiber membranes from many types of polymeric materials such as polyamide, vinyls, and polysulfone and holds the original Michaels patents. These membranes are currently used by the major U.S. auto makers in their electropainting operation to clean rinse waters. Romicon's membranes are also used in electroplating installations, but the number and placement are proprietary information. Initial membrane cost varies from $100,000 to $300,000. Romicon reports that many systems pay for themselves if the recovered material is valuable.[128]

Moderate Demonstration Status (Field Testing)

Bend Research, Inc. is currently field testing a reverse osmosis module that is a hollow fiber with a unique configuration. Reverse osmosis hollow fiber membranes usually have the thin-skin on the external diameter. Feed water flows in through the skin to the center. In the Bend module, the skin is on the inner diameter similar to hollow fiber ultrafiltration membranes. The hollow fiber is made from polysulfone. It is also wider than most, 20-25 mil. This design is believed to eliminate pre-treatment and to reduce fouling. Bend intends to market this membrane within the year under the name of "Concept." Bend estimates the cost to be $10 to $20 per square foot.[129] The module has been field tested successfully in a metal plating shop to recover nickel.[130]

Albany International Membrane Development Venture is planning to introduce a thin film composite hollow fiber membrane made of sulfonated polysulfone. It has been field tested in various applications, including recovery of heavy metal from mining leachate. It can tolerate high temperatures and a pH range

from one to 12. Since this membrane is just becoming commercially available, it was rated at field test status but information on the economics and support technology needed are unavailable.

Low Demonstration Status

Although Abcor membranes were tested extensively to show the feasability of treating electroplating in the 1970's, there are no Abcor installations in the electroplating industry. The membrane that was tested is no longer being manufactured.[131]

Discussions with representatives of UOP (Appendix C) indicated the extent of the use of their reverse osmosis membranes in toxic and hazardous waste water treatment. UOP representatives said that the company has not pursued this application.

Ultrafiltration

High Demonstration Status (Commercially Available)

Abcor makes ultrafiltration membranes in three configurations and uses neutral and charged polysulfone, and cellulose acetate. Abcor membranes have undergone extensive field testing in the area of plating bath wastes. They have no current installations, either ultrafiltration or reverse osmosis systems, in operation.[128] There is one current installation that treats munitions wastes. Abcor has installations in electropainting facilities and in other hazardous waste treatment areas. The cost to treat 100,000 gallons per day was estimated between $250,000 to $500,000.

DYNAMIC AND INORGANIC MEMBRANES

Low Demonstration Status (Laboratory Test Status)

Neptune Microfloc--The HYDROPERM membrane, developed by Hydranautics is an organic polymer dynamic membrane. It is a thermoplastic hollow tube filter which is in the microfiltration range. It has been laboratory tested in electroplating rinse water applications[113] and in treating pinkwater from munitions installations.[132] The system has been field tested on acid lead battery manufacturing waste water.

Lowest Demonstration Status (Some applications in related areas.)

SFEC of France manufactures CARBOSEP, a sintered carbon-based zirconium oxide dynamic filter that can withstand high temperatures and a wide pH range. It is used extensively in the pharmaceutical and dairy industries in Europe. Laboratory work in hazardous and toxic wastewater treatment are currently being investigated in France. Since SFEC has no United States representation, no further information was available.[112] Carre membranes are dynamically formed on stainless steel, either by zirconium oxide (ZOSS) or zirconium oxide polyacrylate (ZOPA). Although these membranes have not been tested in the electroplating industry, they have been field tested in the textile dyeing industry. Dr. Spencer of Clemson University reported that these membranes could be used to treat toxic and hazardous waste waters.[113]

Mott Metallurgical--Lambert H. Mott reported[114] that Mott Metallurgical has no applications in the hazardous and toxic wastewater treatment except in the treating of radioactive waste water from nuclear power plants. Mott's filters are stainless steel, open tubes in the ultrafiltration/microfiltration range. Mott's filters are also used in catalyst recovery.

REVERSE OSMOSIS AND ULTRAFILTRATION SYSTEMS

Three systems have been developed that use membranes to treat hazardous and toxic wastes. These systems combine membranes with other technology in a designed system and examples follow.

High Demonstration Status (Commercially Available)

Memtek (U.S.A.) combines precipitation with ultrafiltration to remove metal hydroxide precipitates from a variety of heavy metal wastes. The ultrafilters use an open tubular design employing polysulfone. Memtek has fifty installations to treat electroplating wastewaters[128] and waters with other metals such as gallium, mercury, fluorides, and arsenic.[134] Memtek has a high demonstration status for hazardous and toxic waste waters. Costs are highly variable depending on the character of the waste.

Moderate Demonstration Status (Field Status)

Memtek of Ontario (no relation to Memtek, U.S.A). has designed a system for Environment Canada that uses a membrane in a mobile reverse osmosis treatment system. The system is designed to treat spills of oil on low energy shorelines and spills of soluble chemicals into small bodies of fresh water. The system desalinates water for steam cleaning of oil from the shoreline and concentrates toxic and hazardous species from spills into small bodies of fresh water. Several membranes were field tested in cleaning leachate from a landfill. The most promising membrane was the Toray PEC-1000 thin film composite membrane made from polyether-polysulfone and formed into the spiral wound configuration.[135] This system has been field tested by Environment Canada.

Texas ROMEC has designed a mobil system to treat oil field wastes, a complex mixture of brine, crude oil emulsions, suspended solids, colloidal particles, and additives. This is a six stage system which includes a Mott Metallurgical microporous metal filter at stage four and a reverse osmosis membrane at stage six. Tests have shown that Toray reverse osmosis membranes to be the most promising of those tested.[136] This system has been successfully field tested and Texas ROMEC is seeking a partner to market the system.

ION EXCHANGE MEMBRANES

Electrodialysis

Moderate to High Demonstration Status

Lancy Laboratories recently purchased the ion exchange membrane technology of Lea Manufacturing. They claim to have proven performance in treating the drag-out from gold, platinum, nickel, tin, copper, silver, palladium, cadmium,

tin-lead, and zinc.[139] The system appears to perform well with most cations except hexavalent chromium. Lancy currently has 43 installations in the electroplating industry. Payback is several months for gold and 1.3 years on the average for nickel. Lancy does not manufacture the membranes themselves, but imports them from Japan. The usual configuration is the stack.[138]

HPD uses the typical electrodialysis stack configuration described under electrodialysis. They have over 70 clients including two in the electroplating industry and one in electronics industry. HPD also cites the use of their membranes to recover acids such as nitric and sulfuric acids.[139]

Ionics uses the typical electrodialysis stack configuration described under electrodialysis. They also have electrodialysis reversal to lower fouling. They use both cellulose and polysulfone resins in their membranes. Although Ionics is the largest supplier of electrodialysis equipment, there is only one Ionics unit in the electroplating industry. Little economic data were available on this.[128]

Ionac manufactures only the membranes for ion exchange. They consist of an ion exchange resin pressed onto an inert polyolefin fabric. Resins are of the same chemistry (divinylbenzene/styrene with sulfonic and quaternary ammonium groups) as described previously.[133]

Lower Demonstration Status

DuPont's NAFION is a perfluorosulfonic acid membrane. One system that has been developed using Nafion in conjunction with an electrode is the COPS or Chromium Oxidation and Purification System. Unlike electrodialysis, only a cation exchange membrane is used between an anode and a cathode. Metallic impurities such as copper, zinc, and cadmium pass through to the cathode, but trivalent chromium does not. It is oxidized to hexavalent chromium by the anode and is restored to the process tank for reuse.[120]

Innova claims to have an electrolytic system that treats hexavalent chromium, the CHROMNAPPER. The system consists of a single, thick ion-permeable membrane. The outside of the membrane is wrapped in a stainless steel mesh cathode and an anode is inserted through the top of the module. This system is not an ion exchanger but an ion transfer medium. They claim to have installations in electroplating industry.[140] They also claim economic advantages to their system. Payback is about two and one half years.[141] They are also introducing a system to remove cations, the CATNAPPER, to remove cation impurities in chrome plating baths.[142]

Rai--Related to electrodiaylsis, is the use of ion exchange membranes as ion exchangers. One system that RAI plans to introduce uses a membrane like a ion exchange resin. The membrane consists of radiation-grafted polypropylene felt, which allows water to permeate, but does not allow the ionic species to pass. This is the opposite of Donnan dialysis. Instead ions are captured onto the membrane to be stripped later by a rotating cathode. The RAI system is becoming available commercially and has been tested in electroplating operations.[119]

LIQUID MEMBRANES

Moderate Demonstration Status

Bend Research has developed a coupled transport supported liquid membrane. The membrane is supported in a module configured similar to the Bend hollow fiber reverse osmosis membrane. Feed water flows through the core of the hollow fiber. Outside the fibers in the module is the liquid membrane into which the ions move. Bend also has swollen gel liquid membranes that are self supporting. Both of these membranes have been field tested for chromate removal and the company plans to manufacture them shortly. Testing is being done on liquid membrane beads. The estimated cost is $1 to $2.50 per one thousand gallons of treatment capacity.[143]

Low Demonstration Status

General Electric has produced a solvent extraction supported liquid membrane. The organic extraction phase is separated from the feed stream by a microporous membrane; likewise, the stripping module is separated from the concentrate with a microporous membrane.[144] This system has been successfully tested with simulated plating rinse waters, but no field testing has been performed. No decision has been made on how or when this membrane will be marketed.[145]

MEMBRANE RESEARCH IN THE MUNITIONS INDUSTRY

Civilian and military personnel were consulted on use of membranes to reduce hazardous wastes from munitions operations. Questions were raised regarding research and knowledgeable persons were asked if they have or would consider membrane technology as a possible technique. Tables 23, 24, and 25 summarize research expertise in this area.

Non-military propellant and explosive industry personnel consulted are listed in Table 23. Personnel conducting research in pollution abatement in the military munitions industry who were consulted are listed in Table 24. The independent consultants and membrane experts who were consulted are listed in Table 25. All of the membrane vendors who were contacted in the course of this project were asked if they knew of any work done in this are using their membranes or others.

Only three studies were identified initially, one performed in 1977 by D. Bhattacharyya, K.A. Garrison, and R.B. Grieves on pinkwater;[146] one on nitrocellulose fines by Curtis Blodgett in 1975 (not currently available); and a followup to the Bhattacharyya paper by Blodgett in 1981.[147]

Bhattacharyya, using a variety of membranes, found the PSAL membrane from Millipore to be effective in treating pinkwater.[146] Several years later, Blodgett tried to follow-up on this work and reported that PSAL was unavailable. Blodgett used bench scale equipment to test hollow fiber, spiral wound and disk type ultrafilters. He found that ultrafiltration, while removing suspended solids and some color, removed less than fifty percent of

TABLE 23

EXPERTS CONSULTED IN THE NON-MILITARY MUNITIONS INDUSTRY

Mr. Price
Plant Manager, Austin Powder
Cleveland, OH

Doug Kilman
Technical Staff, Hercules
Wilmington, DE

Beverly Mohler
Technical Staff, Hercules
Wilmington, DE

Lenonard Smith
Engineer, Hercules
Radford Munitions Plant
Radford, VA

Mike A. Kozak
Engineer, Hercules
Sunflower AAP
Lawrence, KA

Bob Levan
Engineer, Trojan Powder
Salt Lake City, UT

Jeff Codere
Chief Plant Engineer
Ensign Bickford
Simsbury, CT

Jackie Dey
Environmental Affairs
Gulf Explosives
Houston, TX

Engineer
ElDorado Chemical
(formerly a division of Monsanto)
St. Louis, MO

TABLE 24

EXPERTS CONSULTED WHO ARE IN THE

POLLUTION ABATEMENT FIELD IN THE MILITARY MUNITIONS

Bosse Jackson
U.S. Army
Environmental Health Group
Picatinny Arsenal
Dover, NJ

Don Freeman
U.S. Army
Environmental Health Group
Picatinny Arsenal
Dover, NJ

Curtis Blodgett
U.S. Army
Natick Research and Development Laboratories
Natick, MA

Art Kaplan
U.S. Army
Natick Research and Development Laboratories
Natick, MA

Morris Rogers
U.S. Army
Natick Research and Development Laboratories
Natick, MA

Dr. J. C. Hoffsommer
U.S. Navy
Naval Surface Weapons Center
White Oak, MD

TABLE 25

INDEPENDENT CONSULTANTS AND

MEMBRANE EXPERTS CONSULTED ON MUNITIONS WASTES

Richard Baker
Membrane Technology and Research
San Francisco, CA

Dr. D.K. Bhattacharyya
University of Kentucky
Lexington, KY

John Brown
John Brown Consultants
Berkeley Heights, NJ

Herbert Skovronek
Consultant
Morristown, NJ

the TNT from the feed stream. TNT that was removed was not in the concentrate water but was adsorbed into the membrane material, causing serious fouling problems.[147] Blodgett did report that his previous work with nitrocellulose fines showed membranes did effectively remove the fines.[148]

Subsequent discussions with John Brown of John Brown Consultants, an expert in military pollution problems, revealed that research had been conducted using the HYDROPERM dynamic membrane to decolorize pinkwater. Norman Shapira, of Hydranautics had found that although the HYDROPERM filter did not remove all the TNT from pinkwater, it did remove the colored species. Herbert Skovronek, an independent consultant, reported he was aware of some efforts on use of membranes in cleaning up wastewater in ball powder production.

After interviewing the experts listed in Table 23, 24, and 25, it was concluded that there were four reasons why little work had been done in munitions wastes:

- Membranes available at the time were ineffective. Research by Blodgett showed that commercially available ultrafiltration did not remove sufficient TNT from the waste stream to justify further study. Blodgett used three different configurations of membranes and found significant TNT adsorption in the membrane pores.

- It may be dangerous. Some of the non-military people were concerned with the danger of building up a concentrated solution of explosives in the system. Whether these fears are justifiable was not determined.

- The non-military munitions industry under current regulations uses evaporation and open burning to treat hazardous waste streams. Unless current regulations change, there is little interest in investigating pollution control devices.

- The membrane companies do not perceive a market. Since both the military and the non-military industry have shown no interest in the past, membrane companies are not sponsoring research in this area.

Since most of the work done has not been on a large scale, it is hard to say whether the higher shear rates in a larger system might prevent the adsorption and fouling reported by Blodgett. This is a typical ultrafiltration problem that has been overcome in other industries. The choice of reverse osmosis over ultrafiltration might result in better retention of the small organic molecules, such as TNT or RDX, whose molecular weights are considerably less than the ultrafiltration minimum of 300. It was reported by Bhattacharyya[149] that the colored complexes, (Meisenheimer complexes) formed in basic solution by TNT are completely rejected by low pressure composite reverse osmosis membrane. The problems are not insurmountable; however, the question of danger should be addressed. Are there any dangers in building up a concentrate stream of explosives inside a closed vessel under pressure? Some experts, particularly in the non-military industry, are concerned.

The second question is whether further research is desirable since there are competing technologies (activated carbon, surfactants, etc.,) on which much more research has been done and which have a proven efficacy in this area. The demonstration status of this application is virtually non-existent and considerable development effort would be required.

SECTION VI

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